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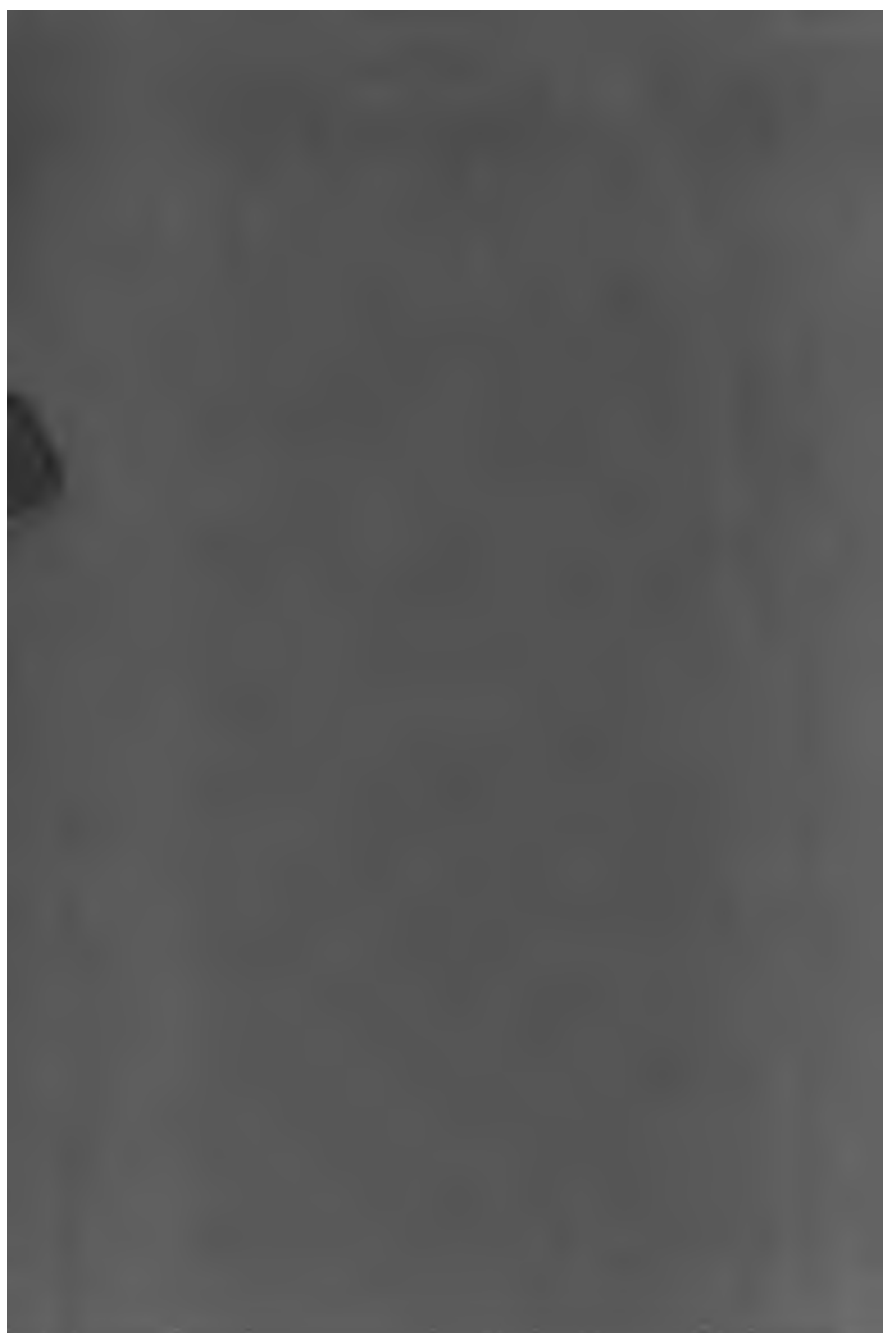
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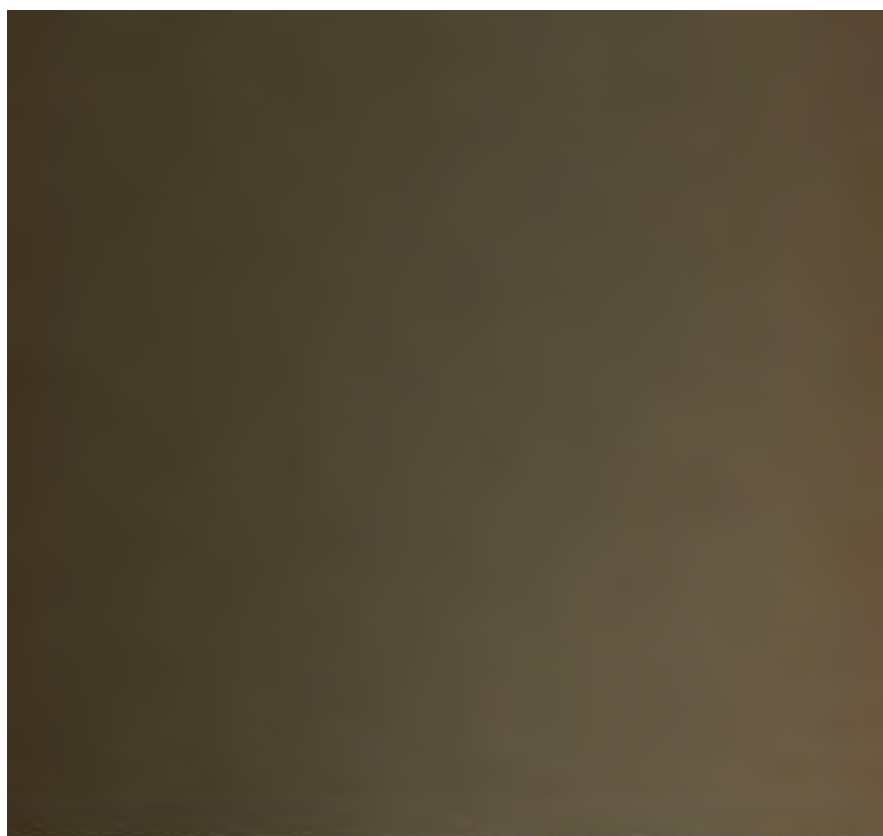
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THE
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A MONTHLY

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AND

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AND THE

Manufacture and Application of Colouring Matters.

EDITED BY

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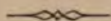
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1. *Notes upon Aniline Black.**

BY M. G. WITZ.

Development of the Calico Printers' Aniline Black observed by the Microscope.—The oxidation of aniline black as it is used in printing when spread in thin layers upon slips of glass and left exposed to the air goes on in the same way as when it is printed on porous, fibrous matters, but more slowly.

I have followed by means of the microscope the gradual formation of the black made with chlorate of potash and vanadium salts, and thickened with starch, such as commonly employed for roller printing, but without any admixture of sightening colours, and both with and without addition of salammoniac.

A few preliminary experiments shewed what thickness of the black should be put upon the glass by the finger. It should not be too opaque, but must have a sufficient body to enable the changes to be seen. The development is much slower than upon cotton.

The examination of the slips of glass, serving simply as a support for the object, by means of polarised light, especially at the outset and before the colour was completely dried, shewed broad, clear, rectangular plates, possessing iridescence, generally at some distance from one another; these are

* Bull. de la Soc. Ind. de Rouen, v., p. 159. Read April 6th, 1877.

chlorate of potash. Besides these there were long crystals like lace or fern leaves in the colour containing salammoniac, and also a striated crystalline mass in abundance shewing an arborescent surface with interlacing branches.

The colours of the crystals are very beautiful when viewed through plates of selenite of varying thickness, but for a continuation of the observation the polarising apparatus may be dispensed with in order to have a stronger light.

After twelve hours in the air at a moderate temperature the characteristic emerald green tint is perceptible to the naked eye, though not visible in the microscope where the dry mass appears as a uniform substance, the highest powers not shewing any green particles, this colour being uniformly diffused over the crystalline mass; the removal of the superficial arborescence allows great numbers of fine separate crystals of chlorate of potash to be seen.

In colour containing salammoniac the green tint is not so equally distributed, and the fern leaf crystallization is specially observable. The muriate of aniline which at first shews numerous crystalline layers lying one above the other would appear to undergo a sort of partial fusion.

Twenty-four hours.—The colour is darker and is particularly observable as a dull green upon the crystalline fractures, probably in consequence of the mechanical effect of the capillarity after absorption of humidity.

Thirty hours.—The green colour is more intense and more uniform; it is not, however, resolvable into any coloured points even with a power magnifying about 1,000 diameters and with a good light, which fact leads to the belief of an extremely fine division of the insoluble colouring matter, while the soluble principles of various natures are contributing to its production. The crystals of chlorate do not seem to be acted upon; they are visible in large numbers even in places where the layer of colour is so thin that the green shade is scarcely developed, and only visible where it is fixed on the transparent and swollen remains of the starch envelopes.

Forty to forty-eight hours.—Not much change; the colour

absorbs moisture, which helps though, slowly, the progressive transformation of the crystallized salts.

The crystals continue to form apparently considerable masses, but they are more confused, especially in the thicker parts where the green colour is strongest.

Fifty-four hours.—The colour is a fine green, which well justifies the old and original denomination of it as *emeraldine*; it has become so dense that light passes through it with difficulty, the mass is uniformly coloured and without points or centres.

During the ageing of ordinary prints the excessively fine particles of insoluble aniline black as they are formed in the colour, are attracted and fixed on the surface, or even within the substance of the porous matter of the fibre. There is, probably, the case of capillary affinity producing dyeing as M. Chevreul has demonstrated in a general manner. In the case of non-thickened liquids the solid particles can only be attracted by one another, agglomerating and forming masses of some degree of coherence. It can be imagined that as by degrees the coloured substance is deposited in the invisible pores of the fibres it adheres to them so closely that the strongest washings cannot displace it.

Sixty hours.—No change.

Very small colourless droplets and signs of crystallization upon the glass, extending beyond the parts covered with the paste were observed; these were afterwards studied.

Seventy-two to eighty hours.—The crystals of chlorate tend to decrease in size and increase in number, their form becoming less regular. The green colour becomes more developed on account of this multiplication of surfaces of contact of the salts.

Ninety-six hours.—By varying the illumination superimposed crystals could be easily recognised; the salammoniac being easily recognized from the characteristic form of its crystals.

The addition of a drop of cold water caused the crystals on the surface to instantly disappear, which are soon reformed by evaporation. Up to this time the greater part of the salts

have taken no part in the reaction, although the whole mass has undergone successive crystalline modifications caused by alterations in the hygrometric state of the paste.

One hundred hours.—Some accessory facts observed several times with powers of 240 to 300 diameters deserve describing.

(1) The drop of water which had penetrated the surface of the colour *without salammoniac*, upon its evaporation has caused masses of crystals, among which could be observed the fern-like shapes which characterise this salt.

(2) The faint, colourless crystalline appearance upon the edges of the slips of glass which have been previously noticed are striated with crossings in many parallel branches. They can only have arisen from the condensation of volatile substances. They are seen to disappear instantaneously at the least breath of air rendered moist by the lungs, and resolve themselves into numerous small drops, arranged with some degree of regularity. They soon go into crystals again spontaneously and suddenly, as if by a kind of explosion giving at once the same appearance as before. The vibration of the air, whistling by drawing in breath between the lips, or metallic percussion sometimes determines the sudden crystallization of dozens of these little drops visible at once in the field of view.

When the absorbed moisture is more considerable, the numberless little drops distributed over the surface of the glass, forming a sort of nebula, increase in size and coalesce in places. Then, when the moisture evaporates, they leave crystals more distinctly of the fern-leaf kind. The slight irregular form which the contours of the liquid globules accidentally assume frequently causes the formation of long crystals extending across the greatest diameter with perpendicular ramifications. Upon this scale the sudden crystallization is quite remarkable. It takes place in several drops at the same time, or in very rapid succession. This phenomenon, though microscopic, seems to be of the same kind as the crystallization of supersaturated solutions. The crystals can be made to redissolve and reappear an indefinite

number of times by slightly varying the temperature and humidity of the surrounding atmosphere. When a large-sized drop, viewed under a power of 300 diameters, is only partly crystallized, it illustrates extremely well the very small forces required to diminish or increase the crystals, and the limit of sensitiveness of this phenomenon is clearly seen.

These facts are useful in order to understand the chemical and physical changes which may be at work during the ageing of prints owing to the mutual actions of the salts contained in the colour. For example, in this particular case, during the formation of the aniline black it is undeniable that there is a slight but continuous evolution of vapours of hydrochloric acid. These meeting the aqueous vapour present in the air condense, and are deposited in an hydrated state in the form of extremely minute vesicles, which cover all the neighbouring parts; afterwards variations in the hygrometric state of the air cause these to unite in small drops isolated one from the other. At the same time the ammonia which naturally exists in the air, although in very small quantity, becomes fixed in these acid drops and produces salammoniac. It is the excessively small parcels of this hygrometric salt which give rise to the appearance observed by the aid of the microscope. To test this hypothesis a drop of dilute hydrochloric acid was left to evaporate spontaneously upon a large piece of glass under the same conditions. After some time the production of similar crystalline forms were observed, and at a relatively considerable distance from the spot where the acid was placed. Whatever may be the admitted explanation of the existence of the ammonia found upon the glass plates, it is evident that the same will serve for the fern leaf crystals observed in the colour to which no salammoniac was added. This salt spontaneously generated under similar conditions helps, by drawing moisture from the air, to cause the partial solution of the other salts, and thus increase the number of points of contact.

This series of experiments was made in the month of April, 1876, in an inhabited room, well ventilated, and free from

smoke and chemical vapours. The experiments were lately repeated to control the observations just recited, for it seemed necessary to examine whether the muriate of aniline was not itself sufficiently volatile at the ordinary temperature to give microscopic crystals having the same appearance as those of salammoniac. The direct method of seeking for the alkaloid in such small quantities of matter being too difficult, it was necessary to have recourse to other methods of investigation.

The amount of humidity in crystals of muriate of aniline can certainly be sufficiently well ascertained by exposing them to a temperature of about 212° . The loss of weight by volatilization of the salt takes place very slowly in comparison with the loss of the excess of water, and acid does not interfere with the accuracy of results which are mainly comparative, and rather for technical than scientific purposes.* But dry muriate of aniline certainly emits a sensible amount of vapour even at 60° F., sufficient to give a yellow colour to shavings of pine. This salt is slowly exhaled from the thickened colours containing it, and its volatilization continues during the ageing or oxidation of the aniline black. This can be well demonstrated by placing a piece of calico which has been dipped in a chlorate and vanadium mixture (without aniline) for some hours at a short distance from blacks while ageing. It becomes covered with a green colour.

When a solution of pure muriate of aniline at 21 oz. per

* Muriate of aniline in crystalline masses, colourless and light, and of very good commercial quality was placed in a 50 c.c. platinum crucible, which it three-quarter fills, and was exposed in a small steam drying chamber to a constant temperature of 216° or 217° F.

The loss of weight representing water and hydrochloric acid amounted to $1\frac{1}{2}$ per cent. after an hour and a half, and did not exceed 2 per cent. in four hours. Afterwards the volatilization of the salt was rigorously determined by five successive weighings at different intervals of time. It corresponded for this temperature to 1 part in 817 of the anhydrous salt *per hour*.

At the commencement of the heating, a slight ring of the salt carried up by the escaping vapour of water was deposited upon the sides of the crucible and did not afterwards disappear; thus it is best to commence the heating gently, and not to have the crucible more than half full of salt.

Muriate of aniline heated for ten hours to 216° F. remains colourless, and forms a colourless solution with water.

gallon is thickened with starch, and then spread on glass, it shews, after a time, by the aid of the microscope, exactly the same appearances round the borders, and at a considerable distance from the colour itself, which were found in the complete black mixture.

But conclusions must not be drawn too hastily from this, for if another thickened mixture be prepared containing only chloride of aluminum, say from such a quantity of pure sulphate of alumina as would be required to exactly precipitate one equivalent of chloride of barium per litre, it will be remarked in about two days that the same kind of small drops, giving striated and crossing lines of crystals, are deposited upon the glass at some distance from the mixture. They are very abundant, and similar in every respect to those which were observed in connection with the aniline black mixture.

In these cases it is really the ammonia normally present in the air which, meeting the moist vapours of hydrochloric acid gradually disengaged from the thickened material, becomes condensed in the saline state in microscopic groups.

When the disengaged vapours contain only muriate of aniline they are also slowly decomposed by the air, and yield salammoniac, as can be demonstrated.

The proof is easy to obtain by subliming either of these hydrochlorates separately from the bottom of a dish, and receiving the vapours upon plates of glass in such small quantity that, when cooled and breathed upon, they become invisible to the eye. Then by viewing the glass plates with a power of 300 diameters, it is seen that the small drops from salammoniac give small crystals with crossings, more or less striated and very hygroscopic. On account of their extreme thinness the forms are not so beautiful as in the formerly-described cases; but the phenomenon of spontaneous crystallization are identical, and can be produced an indefinite number of times at will.

The microscopical crystals which come from the sublimation of the aniline salt are essentially different. They form transparent, isolated points, in some places gathered in

irregular groups ; in other places a dozen of these grains give a sort of crown shape, arising from a larger drop, the centre of which is void. The crystals are invariably isolated from one another in angular grains, the largest of which have a distant resemblance to a star with four unequal points ; they are less hygrometric than salammoniac. The latter is especially characterised by the fact that each little drop gives a single crystalline mass, all the parts of which hold together and are inclined to interlace.

This is confirmed when the last series of plates of glass are subjected carefully to the chlorinated gases disengaged from a chlorate by a dilute acid mixed with a trace of vanadium, when the muriate of aniline is not in too small a quantity upon the glass, it becomes slightly coloured, and has sometimes a purplish reflection. Under the microscope the small isolated crystals appear of a dark opaque green, with indistinct borders, often surrounded with a halo, with a colour gradually diminishing as it increases in size. Many of the crystals have only undergone a superficial change, since they remain still hygroscopic.

The air charged with chlorinated gases acts so energetically upon these very small quantities of matter that it is necessary to regulate very carefully the action and duration of contact, or otherwise the aniline black formed will be immediately bleached. When this happens transparent crystals of simple forms can be seen upon the glass. They are either long needles, formed of prisms laid end to end in a right line, elongated blades, or even oblique rectangular tables.

From these observations it may be concluded :—

(1) That the acid chlorides, like chloride of aluminum and hydrochloric acid, give off vapours which, in the common air, spontaneously form masses of hygroscopic crystals of salammoniac, just the same as the aniline black mixture does. The causes may vary, but the result is the same.

(2) The muriate of aniline is volatile at ordinary temperatures, and with time and under the same conditions gives results identical with the above.

(3) That the salt obtained in microscopic crystals, by means of a hot sublimation quickly conducted, gives forms which differ from those of salammoniac, which may be transformed into black coloured products by exposure to chlorinated gases.

We return now to the older series of observations.

At the end of six days an abundance of small cubical crystals are found upon the surface of the colour, clearly distinct and different from the other salts ; these are doubtless chloride of potassium.

Afterwards there may be seen large and long crystalline plates of a yellowish colour, these are always observed when the production of the aniline black has taken place with sufficient rapidity ; these crystals are volatile, of an unpleasant irritating smell, owing probably to chlorinated quinones, and soon disappear in the air.

We may note in passing that the vanadous chloride, or the hypovanadic chloride crystallized under the microscope in very long prisms, limpid and scarcely blue, grouped together in beautiful stellate masses.

After a time the crystals on the aniline black lose their distinctness, but the appearance of the dark green colouration only changes by becoming deeper. The adhesion of the film of colour formed is so great that friction and pressure of the fingers with the aid of cold water, is not able to detach this varnish-like mass from the glass ; no other thickened colour appears to form so resistant a mass ; it can only be abraded when wet by the nails.

When aniline black is printed upon cotton, it is not easy to find under the microscope any fibres covered with crystals ; some fibres serve to support actual crystalline masses.

In solutions of aniline which are not thickened, the mutual action of the salts is too rapid to be followed ; however, the green colouration when it is observable under the microscope does not appear to be in the form of a precipitate.

In concluding this part we will confine ourselves to drawing

attention only to some consequences to be drawn from this examination.

(1) Aniline black produced by the aid of chlorates in calico printing, appears to be formed *dry* by the close contact of the crystalline salts, there is, however, a modification of the crystals at the surface produced by the absorption of moisture from the air; the formation of chlorinated compounds inferior in amount of oxygen to chloric acid and their possible actions are of course phenomena which cannot be observed under the microscope.

(2) The presence of salammoniac in the colour is not indispensable to the generation of aniline black; but as we have seen there is always production of a certain but exceedingly small quantity of this salt from the ammonia existing in the air.

(3) The chlorate of potash which forms large separate crystals in the dried colour, probably from that fact, does not immediately take part in the reactions, and only acts slowly. The substitution of this salt by the chlorate of aniline which crystallizes in fine needles, and which is an unstable salt, ought, on the other hand, to be favourable to the production of aniline black by printing, which in fact has been found to be the case by many experimenters.

Hypothesis of the nature of the action of vanadium upon the chlorates in the production of aniline black.

Although vanadium only plays an intermediary part in the production of the aniline black, it is the agent which promotes the action of the salts upon one another, and continues it in such a manner that the smallest quantities of the metal suffice to prolong it indefinitely in very large quantities of dye liquors or colours for printing.

So long as chloric acid may be supposed to be present in the acid colour, the vanadium is probably oxidised to vanadic acid, which immediately reacts upon the aniline, oxidising its hydrogen, and forming the base of the insoluble black substance, passing itself at the same time into the lower oxidised state of vanadous oxide; this, in its turn, imme-

diately takes oxygen from the chlorate, and recommences the round of action. The chloric acid, by losing oxygen, forms lower oxygenated chlorine compounds, which are very unstable and very active, themselves it is known assisting in the production of aniline black; so that each molecule of vanadium appears to possess a to-and-fro movement analogous in theory to that of the piston of a pump, by which it is charged rapidly with chloric acid, which it discharges without intermission in a dissociated state of oxygen and chlorinated compounds upon the aniline or other oxidisable substances, or substances which can be dehydrogenated. The amount of this action in a given time is in direct relation with the richness of the mixture in chloric acid, the temperature and the quantity of vanadium, even when this latter appears to be in infinitesimal quantity. The presence of a body to oxidise or dehydrogenise, which absorbs the products formed, also exercises an influence.

At the present time we do not know any other element comparable to vanadium in this property of alternative oxidation and reduction; copper has the same properties, but infinitely less powerful. Oxide of cobalt in very small quantity can decompose an unlimited quantity of boiling solution of bleaching powder, but it is necessary to interrupt the operation and to collect the deposited oxide to make it act upon a fresh portion of substance.

It must not be forgotten that the reaction takes place in a medium constantly acid. Now, vanadic acid, in contact with hydrochloric acid, easily gives rise to chlorine, which is absorbed by the aniline, while the vanadous compound is reoxidised by the chloric acid. Hydrochloric acid itself is generated in proportion as the aniline is converted into the black substance, this accelerates the reaction, notwithstanding the production of insoluble matters.

As to the actual manner in which vanadium undergoes its metamorphoses in the presence of chlorates, it is convenient to propose a new theory, in which the passage into the state of vanadic acid is not necessary; this theory appears to be indicated by the researches of Rosenstiehl upon the action

of chlorate of copper in aniline black. There is a constant tendency to the formation of chlorate of vanadium, a salt which, in a separate state, is extremely unstable; this salt would certainly be more sensitive to oxidisable matters and acted upon at lower temperatures than chlorate of copper. But chloric acid is, according to M. Berthelot, an exothermic body, that is, a body which disengages heat when it acts upon others, in decomposing, by reason of the spontaneous destruction of the chlorate of vanadium, the chloric acid produces more heat than is required for the reaction; the heat is not discernible by physical phenomena, because it is transformed into chemical force, contributing to the decomposition of a fresh quantity, imponderable, it may be said, of chloric acid in combination with vanadium, giving rise at the same time to a continuous production of various chlorinated compounds.

Though there will be still doubts upon what is the real mode of action of vanadium, because by its nature it is difficult to analyse, it must not be forgotten that practically the very valuable properties of this metal are admitted as beyond dispute.

2. *Notes upon the Greening of Aniline Black.**

BY M. F. LAMY.

[*Contents of a sealed packet deposited by M. Lamy at the Industrial Society, October 20th, 1876, and opened at his request at the meeting of January 12th, 1877.*]

IN May, 1873, I presented the Chemical Section of the Society with a Note upon the Greening of Aniline Black, the aim being to give an answer to the following three questions propounded by the section:—

* Bull. de la Soc. Ind. de Rouen, v., pp. 109, 112.

(1) What is the theory of the production of aniline black upon calico?

(2) What causes the black to become green?

(3) What is the best means of insuring the fastness of the black and diminishing the greening of it?

The conclusions of the memoir were:—

(1) Aniline black is formed upon cotton by a progressive oxidation in layers of the aniline.

(2) The greening appears to be owing to influences which take away a certain quantity of oxygen from the black.

(3) The best means of insuring the fastness of the black and diminishing the greening is to assist the intimate combination of the aniline and oxygen. In a word, to promote the oxidation or oxygenation of the aniline.

I also added, "In practice the long exposure of the cloth in a warm and moistened atmosphere to the elevated temperature of about 100° F., the action of bichromate of potash, of alkaline hypochlorites, bleaching powder, even steaming, are the means which may be recommended according to circumstances.

"It is proper to add that the nature of the aniline salt is not without importance; on the one hand as regards the complete fixing of the aniline, and on the other to avoid the serious danger of tendering the cloth."

In the course of my observations I dwelt strongly upon the passage in bichromate of potash after the oxidation or ageing as giving good results as regards the tendency to greening.

Since then I have continued my experiments upon the oxidizing action of bichromate of potash upon aniline black, and I have observed that by treating the black, after it had been sufficiently oxidized in a moist ageing room, by a solution of chromic acid at a certain degree of concentration, it was no longer turned green by the reducing action of sulphurous acid.

My method of operating is very simple:—

After the black has been sufficiently aged—that is, when it has acquired a dark bronze colour—I complete the oxidation by passing it in a bath composed of—

Boiling water	200 gallons.
Bichromate of potash	20 lb.
Hydrofluosilicic acid at 41° Tw.....	20 lb.

Chromic acid is liberated, and the water becomes slightly turbid by the insoluble salt of potash which precipitates. I leave the black in contact with the liquid for one and a half or two minutes, after which I wash and soap at 140° F. for half an hour, wash and dry.

The black thus treated resists very well the action of hydrochloric and sulphurous acid, it is hardly necessary to say that it perfectly resists the action of air and light.

By the same process very fine aniline greys can be obtained, which are no longer liable to be greened by sulphurous acid.

I may remark again, as I did in my first note of 1873, that the kind of aniline salt to be used is not indifferent in order to obtain a complete fixation of the aniline. Although good results can be obtained from the muriate of aniline, I nevertheless prefer the tartrate, this salt permits of a stronger colour being used without danger of injuring the fibre.

The proportion of chromic acid which I have indicated may be modified; thus with 1 part each of bichromate and hydrofluosilicic acid to 1,000 parts of boiling water, and leaving the colours twenty to twenty-five minutes in the bath the same results are obtained; still, I think it is not well to exceed the proportion of 1 part of salt to 100 parts of water, as given in the first instance. If stronger than this the black is injured.

This treatment has not the disadvantage of reddening the black like bichromate alone, for before the soaping it is a pure, velvety, rich black.

Contrary to what has hitherto been observed as to the action of bichromate of potash upon the black, the soaping, even at the boil, does not diminish in the least its fastness, it resists the reducing action of sulphurous acid as well after as before the soaping.

It seems to follow from these experiments that they confirm the conclusions I drew in 1873, when I explained the greening of the black to be due to a disoxygenation of the aniline.

I had completed this study and had put into practice the above method, when various means of unequal efficacy were proposed for preventing the greening of aniline black. The most of them rest upon the choice of the aniline employed, the action of bichromate of potash, and steaming. I had indicated all these means from 1873 as being available for at least retarding the greening. I have further reasons for believing that the papers published in the Bulletin (1873, No. 2) of this society, have been the cause of the researches being taken up by several chemists. I state this, less as a personal claim for priority than as honourable to the Industrial Society at Rouen, and especially to its chemical section.*

3. *Fourth Note upon the Greening of Aniline Black, by the same Author.*†

AT the meeting of January 12th, 1877, the President, at my request, opened the sealed packet deposited by me with the Society on the 20th October, 1876, which contained the preceding note upon the greening of aniline black.

The note, in accordance with the regulations, was openly read by the President, and then committed for examination to the Chemical Section. I think it necessary to make some additions to the contents of the sealed packet which will make it more complete and facilitate its study.

I point out the oxidising action of chromic acid as a means to be employed to render the black unchangeable.

At first sight the process would appear impracticable, for it is well known that a concentrated solution of chromic acid in great measure destroys aniline black, but in a more diluted state the effect is quite the opposite; the black, instead of being destroyed, becomes fuller and richer.

*See M. Lamy's paper, *Textile Colourist*, ii., p. 219.

† Read March 2nd, 1877.

I give some of the methods which I have practised, and first the method pointed out in the sealed packet, which is as follows:—

When the colour has become of a dark bronze shade it is passed at full width in a roller beck containing the following proportion of materials—

200 gallons of boiling water.
20 lb. bichromate of potash.
20 lb. hydrofluosilic acid at 41° Tw.

The hydrofluosilic acid is not indispensable, and in the proportions above indicated can be very well replaced by sulphuric acid, using 4¼ lb. of the concentrated acid to each 10 lb. of the bichromate of potash.

The passage lasts from 1½ to 2 minutes; the goods are then soaped for half an hour, washed, and dried.*

After this passage in chromic acid, if the black has been sufficiently oxidized in the ageing, it will not become green by the action of sulphurous acid. This method, which is satisfactory enough as far as regards the greening, is not all that could be wished for as far as concerns the whites, especially white grounds. To obviate this difficulty I use a second beck with rollers placed in continuation of the first beck or cistern, and charge it with water containing either soda at the rate of 2 lb. caustic at 65° Tw. per 100 gallons, or 5 lb. of quick lime. The second beck is also heated to 212° F., and the piece passed through and the whites much less stained.

There is another method of operating which consists in passing the pieces from the ageing room into a dyebeck which contains for 100 gallons water heated to 212° F., 1 lb. bichromate of potash, and 1 lb. of hydrofluosilic acid at 41° Tw., or instead, 6½ oz. strong sulphuric acid; the pieces are kept in for half an hour, washed, soaped, and dried.

The same methods can be applied to blacks which have

* The proportion of soap to water is stated by the writer as 3 grammes per litre, that would be 3 lb. to 100 gallons water, but evidently that must depend upon the quality of the water, and be left to the discretion of the manager.—*Ed.*

been fixed with carbonate of soda and well washed; the results are the same.

From the practical experiments which I have made, I believe I may state that blacks thus treated with chromic acid in proper proportion resist very well all greening influences. But to succeed there are some points to be attended to, which however are not difficult to hit.

To obtain a good result it is necessary that the black should contain as much aniline as possible, that the ageing be long continued, that the precise quantity of chromic acid required and the length of time necessary in it be known, the temperature being always maintained at the boil.

The tartrate of aniline blacks are to be preferred, as I have previously stated. The aniline black oxidized by chromic acid is somewhat easier acted upon by chlorine than the black fixed by the usual methods.

May it be concluded from what has been said that the question of obtaining an ungreenable black has been solved? It would be bold on my part to answer in the affirmative. There is still something to say and do with regard to this important question, but it may be said now, that what has been done has been in the right direction and towards the object aimed at, and we may hope soon to have commercial blacks which will not become green in warehouses and shops.

4. *Notes from Mulhouse.*

Dissolving of Gum Tragacanth.—At a recent meeting of the Industrial Society of Mulhouse, M. Rosenstiehl made some remarks upon dissolving gum tragacanth. He found by experiment that if a small proportion of hydrochloric acid was added to the water, the time required to prepare a solution of the gum was much less than with pure water. A solution was as well made in four hours this way, as in twelve

or twenty-four hours with simple water, as was usually practised. For say, 20 gallons of water, and 20 lb. of gum tragacanth, he used 8 oz. of hydrochloric acid. This small quantity of acid he says, does no harm in printing, but still as a precaution against possible accidents it is well to add after the solution an equivalent quantity of acetate of soda, 1·4 lb. of crystals of soda, previously saturated with acetic acid, being sufficient to neutralise 1 lb. of hydrochloric acid. By using double the above quantity of acid, that is, taking 1 lb. to 20 gallons of water, a solution of gum tragacanth can be obtained in four hours of the same consistence as would require twenty-four hours maceration without acid.

We may remark upon the communication of M. Rosenstiehl that colour mixers in this country for at least a quarter of a century have known this accelerating action of acid upon the solution of gum tragacanth, and it has been occasionally employed when extra thick gum water was required; the acid preferred was nitric acid, which was afterwards neutralised either by solution of crystals of soda and then acetic acid added, or by acetate of soda at once added. The method is very little used, the preferable way of dissolving gum tragacanth being to leave it soaking for a day or two with occasional stirring, when it quickly dissolves by boiling; but the acid method may be sometimes useful when there is immediate want of the gum water.

We copy the following from a manuscript note book dated 1852:—

Prepared Tragacanth Gum Water.

- 24 lb. gum tragacanth,
- 24 gallons of water, steep twenty-four hours,
- 3 pints nitric acid at 60° Tw.; boil and add
- 6 lb. soda crystals.
- 3 pints acetic acid.

Sulpholeic Acids.—At the same meeting M. Schaeffer drew attention to the sulpholeic acid or sulphated oils, which are now sold under various and fantastic names, as the source of fatty matters in alizarine red printing and dyeing. It was

considered desirable that this body should be studied, and an attempt made to explain what its action was; the study of the question was entrusted to Messrs. Goppelsroeder and Weber.

This modification of oil was first introduced by Mercer and Greenwood in their patent of June 22nd, 1846; but, as far as we know, was not found to possess any advantage over ordinary oil for Turkey red dyeing. Its manufacture has been from time to time revived, and various applications attempted, but without permanent success. Modifications of it are now in use in many places for the production of alizarine red, and it will be of interest to know what the Mulhouse chemists think of it. Several samples have come under our hands in a more or less crude form. One, purporting to be the article discovered by Storck, and sold by Honoré and Co., seems more carefully manufactured than most of the others. It is a perfectly clear oil, shews about 4 per cent. of sulphuric acid when decomposed, and contains ammonia. It is miscible with cold water, and makes a clear solution in warm water. Its base would appear to be mainly castor oil. These sulpho-oils must be distinguished from the so-called soluble oil used mostly as a softener for finishing goods. It is nothing but castor oil soap, which is remarkably soluble in cold water. It is difficult to see what other advantage as a softener, besides its liquid state, it can have over any other kind of soap.

5. *Coloured Discharge on Dip-Blue.*

WE have received the following letter from M. J. Depierre relating to this style:—"I read with much interest in your last number the observations made by M. Koechlin concerning the manufacture of the discharge blue styles. The process which I indicated appears not to be successful upon

dark blue, though the specimens I sent were certainly tolerably dark. (The first and second on p. 222, vol. iii.) It is possible, however, to accomplish the end by the following process, which is entirely new, and which the discoverer, M. Richard, authorises me to communicate to you. The process rests upon the same principles which I pointed out, and consists in padding the blue in a solution of red prussiate of proper strength, and printing upon it the colours as follows:—For white, simply lime water thickened; for colours, magnesia added to the albumen solution and pigment. The goods are steamed in the common way, and washed off. By this method, and adopting the strengths to suit it, the darkest blue can be discharged.”



6. Upon Silk Printing.*

Madder Styles of Silk Printing.—In printing these styles upon foulards the greatest possible attention must be given to the bleaching before printing and the cleansing from the thickening before dyeing.

Bleaching.—The goods are to be boiled, as before stated, with soap and water for the first time during an hour, and a second time for two hours, so as to render the silk as supple as possible, and to remove from it all substances which might attract colour in the dyeing, and which consequently would cause the whites to be bad and the whole print defective. The pieces are then washed in running water, and passed through a beck of water heated at 140° F., then through an alkaline solution made by dissolving 1 lb. of crystals of soda in 10 gallons of water, the object of this treatment being to dissolve out any soap which might remain attached to the

* Abridged from the work of M. D. Kœppelin upon this subject. *Continued from p. 194, vol. iii.*

cloth. The pieces are again washed in running water, and afterwards soured in sulphuric acid marking $3\frac{1}{2}^{\circ}$ Tw., finishing by another washing in running water.

Before treating of the printing, we give the composition of the madder colours, which, properly speaking, consist of mordants thickened so as to be fit for printing.

Black for Madder.

Iron liquor at 11° Tw.....	1 $\frac{1}{2}$ gallons.
White starch	12 oz.
Pipeclay.....	2 $\frac{1}{2}$ lb.
Gallipoli oil	$\frac{1}{4}$ lb.

Red for Madder.

Acetate of alumina at 10° Tw.....	1 gallon.
Acetate of alumina at 18° Tw.....	1 gallon,
White starch	13 oz.
Pipeclay.....	1 $\frac{1}{2}$ lb.
Acetic acid	1 lb.

This mordant may be sightened with a decoction of madder or with a little sulphate of indigo.

Chocolate for Madder.

Iron liquor at 22° Tw.	2 $\frac{1}{2}$ gallons.
Acetate of alumina at 10° Tw.....	10 gallons.
Acetate of alumina at 18° Tw.....	2 gallons.
Logwood liquor at 11° Tw.	1 gallon.
Vinegar	1 gallon.
White starch	8 lb.
Pipeclay.....	15 lb.
Gallipoli oil	2 $\frac{1}{2}$ lb.

Printing.—The foulards are extended in the usual manner upon the printing tables.

The black is first printed, then the ground colour, and lastly the red. In drying care must be taken that the wet parts do not touch one another or the cloth, which would cause "marking off." After drying they are hung in a warm and somewhat moist stove for forty-eight hours, and finally for twelve hours in a quite dry atmosphere.

Cleansing from Thickening.—In this operation it is advisable to work with only a few pieces at a time, so that the

liquors may not become charged with too large a quantity of unfixed mordants. If this happens, the mordants dissolved in the cleansing liquor will combine with the parts of the silk which should remain white, and in the dyeing they would attract colour to a greater or less extent. It is for this reason better to work with a number of small vats, and to prepare each one with a liquor made by boiling 15 lb. to 20 lb. of bran with 40 gallons of water, reducing the temperature to 140° F.

A piece of seven handkerchiefs is immersed in the liquor, keeping the piece as open as possible, and worked in the liquid for ten or fifteen minutes, and then washed in running water with such movement and pressure as will insure the complete removal of every trace of unfixed mordant, for upon this being thoroughly effected depends the goodness of the results.

Sometimes we have commenced by washing the pieces in cold water, and finished the operation by passing in bran as just described; but we prefer the first method of operating, which gives satisfactory results. It fixes a greater quantity of mordant upon the tissue, and the colours are consequently fuller and brighter.

If the print has a very heavy ground of colour, it should have two passages in the bran water instead of one, which in this case is insufficient to fix the colours upon the stuff.

The action of the bran in this process is easy to explain in the following manner. The pieces are hung up in the stoves in order to evaporate away the excess of acids in the mordants, and to induce the formation of sub-salts of alumina and oxide of iron which combine with the stuff; this first action completed, the bran of the cleansing liquid, which contains alkaline and earthy phosphates, as well as albumen and gluten, completes and perfects the precipitation of the bases alumina and iron and their combination with the fibre. It also prevents the excess of mordant, or that portion not in combination with the fibre, and which washes off, from fixing upon the white parts of the handkerchiefs, by means of the phosphates and albumen forming insoluble

compounds which are not absorbed by the fibre. The action of the bran is double; it fixes the mordant upon the printed portions of the goods, and it prevents the white portions from combining with the excess of mordant dissolved off and contained in the liquid.

The Dyeing.—We also recommend that only a few foulards should be dyed at one time, for good results are seldom obtained when working with a large quantity in one dyeing vessel.

In a small beck containing from 7 to 10 gallons of water, boil for a few minutes 11 lb. bran and $\frac{1}{4}$ lb. glue. Reduce the temperature to 95° F.; add $\frac{1}{2}$ lb. sumach, and pass in two pieces of seven handkerchiefs for the space of ten minutes. Then add to the liquor say 1 lb. of garancine which has been steeping for several hours in vinegar, and work the pieces for one-and-a-half hours, raising the temperature to 150° F., and then for another half-hour increasing the heat to about 170° F.; if the colours are not then dark or full enough, the liquor must be raised to the boil and kept at that for some minutes.

The pieces are then washed in running water, and rinsed or beaten until all loose colour is removed. Although the quantity of cloth thus treated seems very small, we prefer as in the cleansing, and for the same reasons, not to operate upon more than seven handkerchiefs at once, and as a single workman can look after several dyes going on at the same time, he is able in the course of a day to do as much work as if he was attending to operations on a larger scale, when he could not manage more than one or two becks at most.

After dyeing it is necessary to proceed to clear the whites, which, notwithstanding all the precautions taken, have become considerably charged with colouring matter. A liquid is prepared by boiling 4 lb. of bran in 10 gallons of water, the temperature being lowered to 170° F., fourteen foulards are entered and worked for about fifteen minutes.

They are afterwards washed in running water, and when well rinsed and cleaned they are passed into water made slightly sour with sulphuric acid or a mixture of sulphuric

and nitric acids, then washed again in cold water, dried, and finished in the manner before described.

Prussian Blue Styles.—Two wooden vats of a capacity of from 35 to 45 gallons are required—the first for the mordant and the second for dyeing.

The mordanting vat is set with the following proportions of material :—

Water.....	15 gallons.
Persulphate of iron at 90° F.	12 lb.
Protochloride of tin	1¾ lb.
Bichloride of tin	1 lb.

Two hundred handkerchiefs are worked in a sufficient quantity of this mordant by means of a wince for five minutes, so that they may be equally impregnated with the mordant. They are then washed and rinsed out in running water, and are ready for dyeing.

The dyeing vat is set with the following proportions of material :—

Water.....	15 gallons.
Yellow prussiate of potash	1½ lb.
Sulphuric acid at 169° Tw.	6 oz.

The pieces are worked in this liquid for four or five minutes, and then washed out the same as after the mordanting.

The process of mordanting, washing, and dyeing, is repeated as many times as may be necessary to obtain the desired shade of colour, which may range from light blue to a shade as dark as indigo. The pieces are then washed and printed with the following discharge :—

Discharge upon Blue.

Caustic potash at 60° Tw.....	8 lb.
British gum	2½ lb.

[*To be continued.*]



7. *Abridgments of Complete Specifications of Patents Recently Published.*

A.D. 1876, October 12th.—No. 3947.

MAGNER, PAUL. "An Improved Process of Treating Vegetable Fibres to impart to them a Silky Appearance." (*Void by reason of the Patentees having neglected to file a Specification in pursuance of the conditions of the Letters Patent.*)

"My invention relates to a process for treating vegetable fibres, such as cotton, flax, hemp, China grass, jute, and the like, to give them a glossy or lustrous appearance, so that they may be used as a substitute for silk, and when manufactured into fabrics will be greatly superior with regard to strength and substance to such fibres in their natural or ordinary condition.

"My improved process is as follows, that is to say, the cotton, linen, or other vegetable fibre is first freed from starchy, and fatty, and extractive matters, and other impurities, by any suitable means, and is converted into binitrated cellulose. For obtaining this product the best method is to employ a mixture of seven volumes of sulphuric acid of a density of 66° Beaumé, and three volumes of azotic acid of a density of 1.420. The cellulose is immersed in this mixture cold for from twelve to fifteen minutes, and the mass is kept in constant agitation so that all parts may be perfectly impregnated with the acid liquor. Then while still moist the binitrated cellulose, which is quite neutral to test paper, is treated with a reducing agent or the like, such as peroxide of hydrogen, bisulphide of hydrogen, chlorine in a nascent state, or by any chemical agent which will give the hydrogen or a portion of the hydrogen that it contains to one or more equivalents of oxygen of the binitrated cellulose to form water. The textile material is then washed and rinsed in boiling water, then in

cold water, and steeped for a few minutes in an acetic or ammoniacal solution of silk or feathers in the following proportions:—One part of solution of silk or 2 parts of solution of feathers for each 100 parts of vegetable fibres.

“For making this solution I proceed as follows:—I introduce 100 parts of acetic acid of a density of 1044 into a digester or other suitable apparatus capable of sustaining a pressure of eighteen atmospheres, then I add 2 parts of silk or 3 parts of feathers, and heat the apparatus till the interior temperature is raised to about 250° centigrade. I maintain the pressure and temperature for about two hours and then allow the apparatus to cool. The solution is then perfectly clear and ready for use.

“The binitrated cellulose after its immersion in the above described solution is placed in an apparatus or vessel wherein a partial vacuum may be produced. (The ordinary extract vacuum pan will be found convenient and suitable for this purpose.) I maintain in the said apparatus or vessel a moderate temperature, say from 60° to 65° centigrade, to dry the fibres gradually. The vacuum or partial vacuum is necessary to free the said fibres after their treatment by my process from the acetic acid or the ammonia which has been employed in the above process and which passes off in the form of gas.”

A.D. 1876, October 27th.—No. 4170.

MOULTON, GEORGE. “Improvements in Apparatus Employed in the Engraving, Milling, or Chasing of Rollers or Cylindrical Surfaces.”

We give only the provisional specification of this patent which will be sufficient to indicate, to those interested, the nature of the invention. The complete specification is accompanied by two sheets of engravings, without which it would not be intelligible.

“My invention relates principally to apparatus employed in the engraving or chasing of metal printing rollers, but is also applicable wholly or in part to apparatus used or suitable for use in the engraving, milling, or chasing of rollers or cylindrical surfaces.

"In certain apparatus the roller to be engraved revolves at the same time that a carriage carrying a cutting tool is caused to traverse, whereby diagonal or spiral lines are cut upon the surface of the roller. Previously to my said invention, motion has been imparted to the said carriage by means of a rack and pinion.

"According to the first part of my invention, I employ a screw in lieu of a rack, and I impart movement to the said carriage by means of a nut which is mounted upon the said carriage and is caused to revolve upon the said screw when the carriage is traversed. A second part of my invention relates to means whereby is effected the 'indexing' which determines the distance apart of the lines cut upon the roller or cylindrical surface.

"According to this part of my invention I employ the said screw and also a shaft which is arranged to revolve in unison with the said nut and which transmits motion to the body to be chased, say for example a copper roller, and I effect the said 'indexing' by rotating the said screw, at the required intervals and to a suitable extent.

"In apparatus which I have devised for the purpose, the said screw is mounted in bearings and the said shaft is also mounted in bearings and arranged in position parallel with the said screw, the said nut being arranged to be rotated by the operator. The said carriage may be guided and sustained by the said screw and shaft alone, or be fitted to slide upon the bed, as preferred. The said shaft is connected by gearing with the said nut, and the shaft is connected at one end by means of gearing or change wheels with a worm which works in a wheel which is connected with the said roller. On one end of the said screw is fixed a worm wheel with which gears a worm which is connected by change wheels with a handle or lever which works in conjunction with a notch plate. A rack is arranged to be actuated by means of a treadle, and when moved in one direction gears with a spur pinion, and thereby imparts movement to the train of gearing which gives motion to the said screw. An incline or part carried by the said rack disengages the said handle from the notch plate

and permits the said motion to be effected. The said rack is moved out of gear with the said pinion before making a return movement. The said rack is guided by means of a piece which is mounted on a fixed stud and is shunted from one to the other of two connected grooves as the said rack commences its acting or its return movement.

“This arrangement may be varied, and if preferred the rack may remain in gear with the said pinion and the latter be fitted to revolve in one direction without actuating the train of gearing. The entire arrangement enables the operator to effect the said ‘indexing’ by simply pressing upon the said treadle with his foot without removing his hands from the handles by means of which he governs the action of the chasing tool.

“The arrangement for rotating the screw may also be employed when milling or when engraving or chasing other than diagonal or spiral lines.

“Other appliances may be substituted for the said treadle, as for example, a sliding rod actuated by hand may give motion to the aforesaid rack, or a revolving rod also actuated by hand may impart motion to the said train of gearing, in which latter case the dividing motion or notch plate and handle may be mounted on the carriage.”

A.D. 1876, October 28th.—No. 4185.

CROYSDALE, WILLIAM. “Improvements in the Means or Apparatus Employed in Dyeing Wool in Indigo Vats.”
(*This invention received provisional protection only.*)

“The object of my invention is to effect a saving of labour and indigo in dyeing wool in indigo vats, and to dispense with the employment of what is known as the nets and bags used in the dyeing and wringing processes.

“I provide a perforated receiver of metal or other suitable material, this I lower into the vat, which has been previously charged with the liquor prepared ready for dyeing; when the receiver is lowered to the required extent into the vat the wool is thrown into it and undergoes the process of dyeing.

"When required the receiver containing the wool may be drawn out of the vat by means of any convenient appliance, such as a crane or its equivalent.

"When the wool is sufficiently dyed the receiver is taken out of the vat and tilted on one side in order to get as much liquor as possible out of the wool and more rapidly previous to its being taken to the wringing apparatus. The tilting operation may be done by any ordinary means.

"A doorway is provided in the side of the receiver through which the operator may pass for the purpose of taking out the wool or for cleansing purposes."

A.D. 1876, November 1st.—No. 4223.

CROSS, JAMES PERCIVAL. "Improvements in the Method of and Apparatus for Singeing Fabrics."

"This invention relates to a method of and apparatus for singeing woven fabrics at the selvages only. Hitherto such fabrics have been singed over the entire surface, or when desired to be singed at the selvages, only this has been very imperfectly performed by hand by means of gas jets and a flexible tube.

"The apparatus may be arranged so as to work either horizontally or vertically. In either case the cloth or fabric passes over and under straightening bars, thence between two sets of gas burners fitted into horizontal tubes placed on each side of the cloth at the selvages only, and then between a pair of drawing rollers which pull the piece of cloth or fabric through the apparatus at the speed desired.

"In the horizontal arrangement the gas jets are placed above and below the cloth, whilst in the vertical arrangement the cloth is caused to pass over a roller above, then vertically through a fire-box placed at each selvage, and thence under a second roller beneath to the drawing rollers.

"Outside each fire-box are two gas pipes, one on each side of the cloth, fitted with jets inclined towards the selvage, and thus the cloth becomes singed at both sides along the selvages only.

"In either case the stop rod of the machine (which is used

for putting the driving strap on to the fast or loose pulley so as to set the drawing rollers in motion or stop them) is connected to levers furnished with hooks which, when the rollers are stopped, pull the selvages out of the fire-boxes at each side, and thus prevent the burning of the cloth. When the rollers are set in motion again the stop rod releases the edges of the cloth, when they again pass into the fire-boxes and the operation proceeds as before."

The above is the provisional specification only; the complete specification is illustrated by two sheets of drawings, without which it cannot be understood.

A.D. 1876, November 1st.—No. 4228.

ROGERS, JAMES HENRY. "An Improvement in the process of Cleansing Woollen Cloths Preparatory to the Dyeing of of the same."

"This invention relates to an improvement in the process of preparing woollen cloths for dyeing and finishing, the object being to effect an economy in the cost of the acid bath employed, to produce a better result, and to render the operation less injurious to the health of the workmen employed.

"Hitherto it has been common (owing to the cost of pure hydrochloric acid) to use, for the formation of the acid bath, the acid used as a bi-product in the alkali manufacture, but this acid, besides being obtained in a very dilute state, necessitating the use of a large number of carboys) contains iron in sufficient quantity to colour the goods submitted to the acid bath to an extent that is very objectionable when light colours are required. Moreover the bath prepared by the use of this acid gives off sulphurous acid fumes, which cause great inconvenience to the workmen employed. Now in order to remedy these inconveniences I prepare a hydrochloric acid bath in which the goods are to be washed or cleansed by combining sulphuric acid with brine or its equivalent in a tank of water. The action of the sulphuric acid upon the brine results in the formation of hydrochloric acid (which will acidulate the water) and in a deposit of sulphate of soda on the bottom and sides of the tank.

"The cloth is to be submitted to this bath and worked in the usual way to cleanse it from the lime or other soaps and other extraneous matters contained in the cloth, after which it is drained or squeezed to express the liquor therefrom, and rinsed in the usual way to remove all traces of the acid.

"Having described in general terms the nature of my invention, I will proceed to give a detailed explanation of the means of carrying out the same.

"In preparing the hydrochloric acid bath I take, say, 45 lb. of sulphuric acid (commonly known as chamber acid) of the specific gravity of 1.600, *i.e.*, 120° Twaddle diluted to 2° Tw., and to this I add about 54 lb. of common salt (chloride of sodium) in crystals; after stirring with a wooden rake until the salt is dissolved, the bath is ready for use. In this bath the cloth is 'worked' either by hand or by any other well known mechanical means until the workman is satisfied, from the appearance of the cloth, that it is cleared of soap, dirt, carbonate of lime, and other extraneous matters. This will take place in somewhat less time than half an hour, the bath being in good condition and the cloth of an average thickness. It is then drawn out of the bath by means of a winch, the liquor with which it is saturated being at the same time squeezed out by means of nipping rollers. The cloth is next washed with water in a washing machine to remove any remaining acid therefrom, after which it will be in a fit state for dyeing if that is required, or for finishing in any of the various ways well understood.

"In cases where the residual liquor is allowed to become a saturated solution by additions of the above ingredients, and by the return of the liquor expressed from the cloth on its removal from the bath, sulphate of soda will deposit on cooling the bath, together with sulphate of lime and other matters removed from the cloth. By separating these matters from the sulphate of soda, that substance may be utilized as a marketable product.

"The method of using the bath which I prefer after the removal of the first piece of cloth, is to renew the hydrochloric

acid by the addition of sulphuric acid and common salt before mentioned, taking care that the latter is added in excess, *viz.*, more than 59 parts of salt by weight to 49 parts by weight of sulphuric acid. This excess of salt is to avoid the presence in the liquor of uncombined sulphuric acid.

"If the pieces are not too bulky nor too dirty, 6 lb. of sulphuric acid and 8 lb. of common salt form a suitable charge to keep up the strength of the hydrochloric acid bath from piece to piece.

"When the action of the bath is to be accelerated, I heat it by steam or in any other well known manner.

"I would remark that the hydrochloric acid, when generated in the bath as above explained, is far more efficient than when mixed with water in the ordinary manner. Moreover the nascent gas is absorbed by the liquor, and no inconvenience is experienced from the escape of acid fumes.

"The sulphate of soda formed in the bath, although taken up by and partially retained in the cloth, is not detrimental thereto, but is rather advantageous when the cloth is to be dyed, as it acts the part of a mordant in preparing the cloth for the dye.

"Another advantage incidental to the invention is, that the strength of the cloth is materially increased by being subjected to this cleansing process, experiments having proved that on an average the tenacity of the cloth is increased by some fifteen per cent.

"Having now set forth the nature of my invention, and explained the manner of carrying the same into effect, I claim, the cleansing of woollen cloths by submitting the same to a hydrochloric acid bath prepared as above described, in which the nascent acid gas is brought into contact with the goods."

A.D. 1876, November 8th.—No. 4318.

GAUDCHAUX-PICARD, EMILE. "Improvements in Chemically Unweaving Textile Fabrics made of Animal and Vegetable Fibrous Substances for the Purpose of Utilizing by Combing Silk or Wool Filaments therefrom."

"In the processes heretofore employed for separating the animal fibre from the vegetable fibre in waste textile fabrics containing a mixture of both kinds of fibre for the purpose of utilizing the wool or silk filaments thereof, it has been necessary to tear or cut the fabric into very small pieces in order to obtain the above-named filaments in the necessary separated condition, and by this means the filaments were reduced to such a small state that they were of little or no value for being used again in the manufacture of fabrics.

"My present invention has for its object to obtain these wool or silk filaments separated from the fabric of their full length so as to render them applicable to the processes of carding, combing, and the like, whereby they may be rendered available for being again manufactured into threads, yarns, fabrics, or felts. For this purpose I firstly sort the waste fabrics so as to separate therefrom those pieces in which either the warp or the weft is wholly of animal fibre, while the weft or the warp is wholly of vegetable fibre, and I make use only of those pieces, rejecting all those in which the two descriptions of fibre are contained both in the warp and the weft. Such sorted pieces I then subject to what may be termed a chemical process of unweaving, that is to say, I destroy the warp or weft of vegetable fibre by treating the fabric with sulphuric, nitric, or hydrochloric acid, or with any other known substance that will destroy vegetable fibre, but will not act upon animal fibre; but by preference I employ for this purpose hydrochloric acid gas in a dry state. After washing or even without being washed the fabric so treated is reduced to such a state of disintegration that by simply rubbing or slightly beating it the vegetable matter will fall from it in a state of powder, leaving the wool or silk warp or weft in its entire condition, in which it can then readily be subjected to the combing or carding processes or to other well known operations for converting the fibre into threads, yarns, fabrics, or felts.

"My above described process of sorting the pieces of fabric and then chemically acting upon only those pieces that contain animal fibre in the warp or weft only has therefore

the effect of obtaining the animal fibres therefrom in a perfect and separated condition, and consequently of much greater commercial value than is the case where the animal fibre obtained is still an interlaced condition owing to its existing both in the warp and the weft of the unsorted pieces of fabric, inasmuch as in the latter case in order to obtain the fibres in a separated condition it is necessary to tear or break them to a very small size of little or no value for the purpose of weaving, whereas in the former case the fibre is produced in such a state that it can at once be utilized for spinning and weaving.

“Having thus described the nature of my said invention, and in what manner the same is to be performed, I claim, the before described method of chemically unweaving fabrics composed of animal and vegetable fibre by first sorting out the pieces in which the animal fibre exists in the warp or the weft only, and then chemically operating upon these pieces so as to destroy the vegetable fibre, and thus obtain the animal fibre in an entire and separated condition suitable for being subjected to the combing, carding, drawing, and other operations.”

A.D. 1876, November 8th.—No. 4321.

KNOWLES, SAMUEL. “Improvements in Conditioning and Ageing Printed Fabrics, and in Apparatus Employed therein.” (*Void by reason of the Patentees having neglected to file a Specification in pursuance of the conditions of the Letters Patent.*)

“My improvements in conditioning and ageing printed fabrics consist in forcing by means of a fan or otherwise a current of air, either cold or heated, into the chamber through which the fabric to be operated upon is conveyed. This chamber may be heated by steam chests or not as may be required. The fabric is traversed backwards and forwards in the chamber so as to expose it to the air for the required time. It is then taken into an upper chamber and carried over and under guide rollers. The air from the lower chamber enters the upper chamber through openings. The

vapours and gases which escape during the process, are drawn off by a fan or other equivalent.

"When necessary, jets of steam may be introduced into the chambers to condition the fabric or to accelerate the process of ageing."

A.D. 1876, November 9th.—No. 4340.

DREYFUS, CHARLES. "Improvements in Dyeing and Printing." (*This invention received provisional protection only.*)

"These improvements consist in producing aniline blacks which will much better stand the action of the air and light than the blacks hitherto produced.

"To carry out this invention I take the aniline black dyed or printed on textile fabrics or yarns, after having been aged or oxidized and raised by any of the operations well known to dyers and printers. I then pass it through a beck containing water, to which I add a solution of an aniline violet, in preference a red shade of violet, but any other violet derived from coal tar will answer the purpose. The black in passing through these solutions, which may or may not be heated to the boiling point, absorbs the violet colouring matter, and the black so produced will stand much better the action of air and light than the black which has not been passed through such a bath, and will not turn green so soon."

A.D. 1876, November 16th.—No. 4435.

DEWHURST, HENRY, of Huddersfield, in the county of York. "Improved Means or Methods of Embossing, Indenting, or Engraving Shapes and Designs on Woven or Felted Fabrics."

"The object of this invention is to imitate fancy or figure weaving on woven or felted fabrics, and the means or methods employed to attain this object consist in applying solvents of fibrous materials to the fabric by means of an ordinary engraved printing roller, block, or stencil plate. The solvents may consist of alkaline chemicals, such as caustic soda, caustic potash, or any of the soda and potash salts, either combined or separately; also an alkaline solution of copper, such as may be obtained by dissolving oxide of copper in a solution of ammonia. When the roller, block, or plate is brought into

contact with the fabric, the figure or design is printed or impressed thereon with the solvents above referred to, such solvents eating or decomposing those parts of the material impressed therewith, the result being that a clear, distinct, and permanent figure or design is produced on the fabric.

“To facilitate the eating or decomposing of the material impressed with the solvents the fabric is exposed to the action of steam.

“In applying my invention to woollen or worsted fabrics, I use a solution of caustic soda, caustic potash, or a mixture of these, but preferably a solution of ordinary caustic soda of 35° Twaddle, or specific gravity 1.175 for an ordinary engraved roller or block; but I vary the strength of it according as it is required for deeper or lighter engraved designs. I mix the aforesaid solution of caustic soda with mucilage of Irish moss as a thickener or vehicle, I then print the said thickened mixture of caustic soda on woven or felted fabrics either previously dyed or in the ‘grey,’ using an ordinary printing roller, block, or stencil for that purpose; I then dry the goods either by passing them over hot cylinders or chests, or through a chamber of hot air until the thickened mixture of caustic soda is dry or set; I then steam the goods in the ordinary way. When the pressure of the steam is about 50 lb. per square inch in the boiler, I find that ten minutes steaming with 2 or 3 lb. pressure in the steam chest or chamber is sufficient to develop the design. When the goods come out of the steam chest or chamber the design is found to be formed on the fabric by the solvent or destructive action of the caustic soda upon that portion of the fabric on which the design has been printed, impressed, or stencilled. If the design is not fully indented or developed I continue the steaming until I find it sufficiently done; the goods are then washed to remove the caustic soda or other solvent, and further treated by dyeing or otherwise in the ordinary way.

“For cotton fabrics I use a solution which has a solvent action on cotton, made by saturating a strong solution of ammonia with oxide of copper; this I stiffen or thicken with a solution of glue or other suitable substance; I then print with

this mixture and steam dry, and wash them in the manner hereinbefore described as applied to woollen goods.

"Having thus described the nature of my invention, and the manner in which the same is to be or may be carried into practice, I would have it understood that I do not confine myself to the use of the chemicals herein described, as various other solvents of animal and vegetable fibres may be used with more or less success; but what I claim as my invention and consider to be new is,—

"Firstly. The use of caustic soda, caustic potash, or mixtures of these, or mixtures of one or both of these with salts of soda, or potash, or other solvents of animal fibres for the purpose of embossing, indenting, or engraving shapes and designs on woven or felted fabrics when applied in the manner herein described.

"Secondly. The use of the herein described ammoniacal solution of oxide of copper or other solvent, of vegetable fibres applied in the manner and for the purpose herein described."

A.D. 1876, November 20th.—No. 4483.

BROCHOCKI, Comte THOMAS DE DIENHEIM. "The Manufacture of Concrete Substances or Products to be used as a Substitute for Lye or Javelle."

"Alkaline hypochlorites in a liquid condition, which have received various names, such as lye of Javelle or Labarraque liquor, are considered perfect as bleaching materials.

"This invention relates to the preparation of these substances in a solid condition, either crystallized or granular, or in cake, in the following manner:—A concentrated alkaline lye of soda or potash is cooled, and through it is passed a current of chlorine gas previously cooled and washed in cold water until the lye becomes almost completely saturated, being kept cool throughout the operation by the immersion of the vessels employed in a bath of water, which is kept at a low temperature, not exceeding 50° Fahr. At the end of about 24 hours there is obtained a crystallized product possessing powerful bleaching properties. The mother liquor

concentrated by evaporation in vacuo being again cooled will furnish an additional quantity of the crystals.

“Another method is to pass a current of chlorine over a thin layer of alkaline carbonate, spread over surfaces kept cold in a close vessel. The chlorine issuing from this vessel is passed through a very strong lye of oxide of the same alkali as that in the carbonate, and this lye kept constantly cool readily absorbs the chlorine, producing hypochlorite. By a lateral opening that can be hermetically closed fresh quantities of carbonate are introduced into the first vessel from time to time when the material therein is supposed to be nearly saturated, and thus the risk of decomposition is avoided. The liquid hypochlorite produced in the second vessel being mixed with the partially saturated carbonate in the first there is obtained a new product, which is solid and crystalline, the carbonate taking up the water of the hypochlorite solution, so as to fix the hypochloric acid in a solid form and in quantity depending on the proportions in which the liquid hypochlorite and the partially saturated carbonate are mixed together.

“For the purpose of solidifying the hypochlorite solution the carbonate may be used without being in the first place exposed to chlorine, and other substances that take up water may be employed for the same purpose, but in such cases the product is less strong in chlorine.

“The concrete product obtained by either of the methods above described is white in colour, but may be coloured as desired. It retains its bleaching properties longer than any of the liquid hypochlorites. It may be prepared for commerce in the condition of a granular salt by merely agitating the solution, when it becomes pasty, or in cakes by running the pasty mass into moulds and allowing it to solidify at a low temperature, the mould, being for that purpose iced. It can be easily packed and transported, as in the solid condition it does not affect metals nor organic substances. For use it is dissolved in cold water with facility.

“Having thus described the nature of my invention, and in what manner the same is to be performed, I claim—

"First. The manufacture of alkaline hypochlorite bleaching material in concrete form by passing chlorine through concentrated alkaline lye maintained at a low temperature, and continuing the treatment until crystals of the said hypochlorite are produced, substantially as herein described.

"Second. The manufacture of concrete bleaching material by passing chlorine through concentrated alkaline lye till an alkaline hypochlorite is obtained in solution, and solidifying the same by the addition of the alkaline carbonate, substantially as herein described.

Third. In manufacturing concrete bleaching material by the method referred to in the preceding claim, the use for solidifying the hypochlorite solution of alkaline carbonate which has previously been exposed in a thin layer to the action of chlorine, substantially as herein described."

A.D. 1876, December 20th.—No. 4912.

WILSON, WILLIAM VIRGO, and CANT, HEMINGTON. "Improvements in the Manufacture of Aniline Dyes."

"In the manufacture of rosaniline or red aniline dye certain secondary products are simultaneously obtained, among these occurring chrysaniline and chrysotoludine, yellow dyes known in commerce as phosphine and other resinous products.

"The object of our invention is the separation of these associated bodies from the red dye, and we effect this by first treating the crude red melt with a caustic alkali or alkaline earth, in practice however preferring caustic soda, and we thus obtain the colouring matter in a basic form.

"When the above process is complete the resulting bases must be washed and dried, and then submitted to the action of commercial benzol, either in the cold or by heat, without pressure, or preferably with pressure, when after a sufficient digestion with this reagent, that is, when the foreign matters are to a great extent dissolved, the insoluble rosaniline base, now in a high state of purity, is collected upon a filter, and can be at once employed for the manufacture of magenta crystals or other well known dyes by the usual processes.

"Commercial benzol is always associated with its higher

homologues, which also have a solvent action, but for the purposes of this invention we prefer that known as 90 per cent. benzol.

"The vessel in which the operation is conducted may be of iron or copper or other suitable material, and so enclosed as to prevent the loss of any appreciable quantity of the solvent.

"Bye-products and residues resulting from the manufacture of aniline dyes may also be similarly treated.

"Having thus described the nature of our invention, and the method of performing the same, we would have it understood that we claim the use of benzol for the purification of red aniline dye in the manner above described.'

8. *British and Foreign Patents, from the Commissioners of Patents Journal, May 25th to June 22nd, 1877, inclusive.*

Rollers, Bleaching and Scouring.

185,377. T. WHITEHOUSE, of Boston, Mass., assignor to the American Tube Works, of the same place, for "Manufacture of copper print-rolls."—Application filed August 3rd, 1876.—American patent.

Claim.—"1. A hollow or tubular metal roll, having its inner side or periphery made with a spline or rib, or other equivalent construction, by a compression of the metal which composes the body of the said roll. 2. A hollow or tubular metal roll, having its inner side or periphery of a taper from end to end, and made with a spline or rib or of other equivalent construction, by a compression of the metal which composes the body of the said roll. 3. The manufacture of a hollow or tubular metal roll, with a spline or rib or other equivalent device upon its inner side, by passing the metal which makes the body of said roll, in conjunction with an internal mandrel or former of suitable shape, between grooved pressure-rolls, all substantially as described, and for the purpose specified."

1900. ADOLPH ALEXANDRE PLANTRON, jeune, of Boulevard de Strasbourg, 23, Paris (France), Director of Manufacture, for the invention of "An improved process of scouring and purifying vegetable and animal fibres and fabrics.—Provisional protection has been granted.

2067. HENRY BARKER WINGETT, of High Street, Alton, in the county of Hants, for an invention of "Improvements in bleach-

- ing paper-pulp, textile fabrics, and other fibrous material."—Dated 26th May, 1877.—Provisional protection has been granted.
- 115,926. KNAB and FOURNIER, for "Bleaching wool, silk, &c."—Dated 9th December, 1876.—French Patent.
- 42,220. A. A. PLANTROU, for an imported invention of "Scouring and purifying textile substances at once."—Dated 14th May, 1877.—(French patent, 20th April, 1877.)—Belgian patent.

Obtaining and Treating Colours, etc.

4839. CHARLES GIRARD, EDMOND WILLM, and GUSTAVE BONCHARDAT, all of Paris, in the republic of France, for an invention of "Improved processes for obtaining colouring matters or of processes for obtaining novel colouring matters."—Dated 14th December, 1876.—This patent has passed the great seal.
674. MICHEL EDMOND SAVIGNY, Chemist, and ALFRED CHARLES COLLINEAU, Doctor in Medicine, both of Boulevard St. Denis, 1, at Paris, have given notice to proceed in respect of the invention of "The manufacture of an improved vegetable colouring substance, and the derivatives thereof."
1056. WILLIAM JACKSON, of Urmston, near Manchester, in the county of Lancaster, Print Buyer, for an invention of "Improvements in treating fabrics printed with aniline colours."—Dated 16th March, 1877.—New application.
2071. CARL RUMPF, of New York, in the state of New York, United States of America, but at present residing at Glasgow, in the county of Lanark, North Britain, for an invention of "A new or improved dry process of oxidising 'anthracene,' and improvements in the manufacture of dyes and other colouring matters from the product so obtained."—Partly his own invention and partly a communication to him from abroad by Friedrich Bayer, Friedrich Westcott, and August Siller, all of Barmen, Rhenish Prussia.—Dated 15th June, 1874.—This patent has become void.
2009. JOHN CASTHELAZ, of Crumpsall Vale Chemical Works, near Manchester, in the County of Lancaster, Manufacturing Chemist, for an invention of "Improvements in the preparation of products of aniline and matters from which aniline is or may be derived, suitable to be used in dyeing and printing, and in the preparation of colouring matters."—Dated June 10th, 1874.—This patent has become void.
7429. WM. M. BROWN, of London, England, assignee of John

Lightfoot, for "Dyeing and printing textile fabrics."—Patent No. 111,654, dated 7th February, 1871.—Application filed 28th August, 1876.—Re-issue.

Claim.—"The method of preparing color-mixtures for aniline black, by producing chlorate of soda and combining therewith a salt or salts of aniline and a suitable metallic salt, substantially as described."

7430. WM. M. BROWN, of London, England, assignee of John Lightfoot, for "Dyeing and printing textile fabrics."—Patent No. 111,654, dated 7th February, 1871.—Application filed 6th December, 1876.—Re-issue.

Claim.—"The method of preparing color-mixtures for aniline black, by producing chlorate of ammonia and combining therewith a salt or salts of aniline and a suitable metallic salt, substantially as described."

7431. WM. M. BROWN, of London, England, assignee of John Lightfoot, for "Dyeing and printing textile fabrics."—Patent No. 111,654, dated 7th February, 1871.—Application filed 6th December, 1876.—Re-issue.

Claim.—"A color-mixture for aniline black, containing as active constituents a salt or salts of aniline, an alkaline chlorate, or other suitable oxidizing-agent, and vanadium, or one of more of its salts, oxides, or sulphides."

7432. WM. M. BROWN, of London, England, assignee of John Lightfoot, for "Dyeing and printing textile fabrics."—Patent 111,654, dated 7th February, 1871.—Application filed 6th December, 1876.—Re-issue.

Claim.—"A color-mixture for aniline-black, containing as active constituents, a salt or salts of aniline, an alkaline chlorate, or other suitable oxidizing agent, and uranium, or one or more of its salts, oxides, or sulphides."

The four preceding patents are re-issues of the original United States patent.

- 184,142. SAMUEL CABOT, Jr., of Boston, Mass., for "Processes of manufacturing anthracene."—Application filed 31st October, 1876.—American Patent.

Claim.—1. The process of manufacturing anthracene or other heavy hydrocarbons, consisting, essentially, in injecting into the still a vapor having less latent heat than steam to raise anthracene or heavy hydrocarbon out of the still or retort, substantially as and for the purpose set forth.
2. The process of manufacturing anthracene or other heavy hydrocarbons, consisting in first vaporizing any of the petroleum ethers or other light hydrocarbons by passing the same through pipes or other vessels located in close proximity to the still, and then injecting said vapors into the still for the purpose of raising anthracene or any heavy hydrocarbon out of the still, substantially as set forth."

67. R. SIMPSON, A. BROOKE, and T. ROYLE, of Greenford Green, Middlesex, for "Improvements in preparing alizarine and other colouring substances extracted from anthracene."—14 years.—Dated 12th February, 1877.—Italian patent.
- 42,111. G. WOLFF, for "Mixtures for colouring the products of aniline."—Dated 3rd May, 1877.—Belgian patent.
- 116,229. SAVIGNY and COLLINEAU, for "Preparing a vegetable colouring substance, thoroughly innocuous, called 'cauline,' and its sub-products."—Dated 29th December, 1876.—French patent.

Processes of Printing and Dyeing.

266. JAMES CHADWICK, of the Spring Brook Print Works, Chaderton, in the county of Lancaster, has given notice at the Office of the Commissioners of his intention to proceed with his application for Letters Patent for the invention of "Improvements in printing textile fabrics."—A communication to him from abroad by James Harley, of Lowell, Massachusetts, United States of America.
2108. JOHN KNOWLES, of Globe Works, Manningham, near Bradford, in the county of York, Machine Maker, for an invention of "Improvements in securing rollers in dyeing and sizing machine vats."—Dated 30th May, 1877.—Provisional protection has been granted.
2197. HENRY DEWHURST, of Huddersfield, in the county of York, Woollen Printer, for an invention of "Improvements in mordanting or preparing woven or felted fabrics for printing."—Dated 6th June, 1877.—Provisional protection has been granted.
2399. THOMAS PATERSON MILLER, of the Cambuslang Dyeworks, in the county of Lanark, North Britain, for an invention of "Improvements in or connected with the process of dyeing yarn or cloth with alizarine or analogous coloring matters."—Dated 21st June 1877.
1756. SAMUEL MILNE SMITH and CHARLES TELFORD SMITH, of Horton Dye Works, Bradford, in the county of York, Dyers and Finishers, for an invention for "Improvements in dyeing or printing textile or other fabrics, warps, or yarns, and in machinery and apparatus to be employed therein."—Dated 18th May, 1874.—This patent has become void.

- 115,864. PRAT, for "A spiraloid tenter for dyeing stuffs in pieces or parts."—Dated 5th December, 1876.—French patent.
- 116,231. SIX, for "Printing velvet in pieces."—Dated 28th December, 1876.—French patent.
- 116,242. ZINGLER, for "Improvements in preparing albumen of blood and applying it for dyeing and printing tissues and other substances with colours, and also for sizing and enamelling wood, glass, and metals."—Dated 28th December, 1876.—French patent.

Drying.

2787. The Letters Patent granted to WILLIAM HARPER, of the firm of Messrs. Eden and Thwaites, of Bolton, in the county of Lancaster, Bleachers and Finishers, for an invention of "Improvements in machinery or apparatus for suspending fabrics in drying stoves," dated 25th September, 1869, and advertised in the Commissioners of Patents' Journal of 6th October, 1876, (and *Textile Colourist*, vol. II., p. 294), as having become void by reason of the non-payment of the additional Stamp Duty of 100*l.*, have been stamped with the additional Stamp Duty of 100*l.*, and were produced at the Office of the Commissioners of Patents for Inventions on the 11th day of June, 1877, pursuant to the Act 40 Vict. c. 19, intituled "An Act for rendering valid certain Letters Patent granted to William Harper for 'Improvements in machinery or apparatus for suspending fabrics in drying stoves.'"
20. C. H. WEISBACH, of Chemnitz, for "Rotary engines with an air-current for drying yarn."—3 years.—Dated 28th December, 1876.—Italian patent.
79. C. H. WEISBACH, of Chemintz, for "A rotary machine with a ventilator for drying yarn."—2 years.—(Secret.)—Dated 22nd January, 1877.—Austrian patent.
- 115,809. TULPIN, Brothers, of Rouen, for "A continuous mode of drying textile substances by the suction of hot air through the layers."—Dated 20th November, 1876.—French patent.
- 115,938. TESTUD DE BEAUREGARD, of Paris, for "A drying-room for fabrics."—Dated 12th April, 1876.—French patent.

Yarns, Skeins.

1548. JOHN DARGUE and WILLIAM DARGUE, of Bradford, in the county of York, Machinists, for an invention of "Improvements

in machinery or apparatus employed in the process of bleaching, scouring, dyeing, and sizing warps or yarns and fabrics."—Dated 27th May, 1870.—This patent has become void.

- 115,884. DURANÇON, for "Improvements in machines for washing textile substances in skeins."—Dated 7th December, 1876.—French patent.

Wool and Silk Treatments.

4923. ALEXANDER MELVILLE CLARK, of 53, Chancery Lane, in the County of Middlesex, Patent Agent, for an invention of "Improvements in the treatment of wool and apparatus for the same."—A communication to him from abroad by Jules Raulin, Professor of Chemistry at the Faculty of Sciences, of Lyons, France.—Dated 20th December, 1876.—This patent has passed the great seal.
1905. ADRIEN ENOULT, of Elbeuf-sur-Seine, in the republic of France, for the invention of "Improvements in machinery or apparatus for removing knots from woollen and other textile fabrics and for dressing and finishing the same."—Provisional protection has been granted.
2208. ANDRE PROSPER ROCHETTE, of Petit-Quevilly, près Rouen, in the republic of France, for an invention of "Improvements in washing wool."—Dated 6th June, 1877.
- 184,301. C. G. SARGENT and F. G. SARGENT, of Graniteville, Mass., for "Wool-washing machines."—Application filed 19th July, 1876.—American patent.

Claim.—"1. In a wool-washing machine, the combination of a bowl or tank A, press-rolls B, an inclined table C, and a single reciprocating carrier D, substantially such as shown and described, constructed and arranged to deliver the fiber from the bowl to the rolls without assistance. 2. In a wool-washing machine, the combination of the table C and the reciprocating toothed carrier D, provided with hooked rear arms R, substantially as shown. 3. The combination of the swinging-arms E, retarded in their movement, with the vertically sliding carrier D mounted thereon and connected by devices, substantially as shown and described, with the pitman M, whereby the carrier is caused to rise and fall as it moves backward and forward, as set forth. 4. The combination of the shaft F, provided with the arms E and the pulley H, encircled by the friction-strap I, the vertically-sliding carrier D, mounted on the arms E, the rock-shaft J provided with the arms K and L, and the pitman M and crank N, arranged to operate as described. 5. In combination with the pitman M, arranged to operate as shown, the toothed bar or rake Q, secured rigidly thereto, as shown. 6. The raised toothed ribs S, constructed and arranged substantially as and

- for the purpose described. 7. The elastic or spring teeth U, secured upon the face of the table C, as shown, to prevent the backward movement of the fiber. 8. The spring-arms T, arranged above the face of the table, substantially as and for the purpose described. 9. The pivoted carrier-teeth *d*, provided with the notches *e* in their lower ends, as shown and described. 10. In combination with the pivoted teeth *d*, and the bar *i*, having its ends mounted on springs, as shown, and for the purpose described. 11. In a wool-washing machine, a reciprocating carrier D, provided with elastic wire teeth F, as described. 12. The combination of the table C, provided with the raised ribs S, and the carrier D, provided with the teeth *g*, having their ends curved forward, as shown. 13. In combination with the doffer-roll W, the guards X, constructed and arranged substantially as shown, and for the purpose described."
- 115,970. SAVARY, for "A product for dyeing wool blue, black, green, or maroon."—Dated 12th December, 1876.—French patent.
- 116,043. CHALAMEL and Co., for "A process of dyeing woollen tissues with aniline black."—Dated 18th December, 1876.—French patent.
- 116,150. IMBS, for "Treatment of threads of single raw silk after dyeing."—Dated 22nd December, 1876.—French patent.
- 116,239. WASTIAUX, sen. and jun., for "A chemical process for cleaning and disacidifying wool, woollen rags, and tissues."—Dated 29th December, 1876.—French patent.
55. J. A. C. NOGARET and P. F. BOUSQUIER, of Saint Jean du Gard, for "An economical system of regulating the scouring of silk."—5 years.—Dated 16th January, 1877.—Italian patent.

Finishing Processes.

859. JOHN WILSON, of the firm of John Wilson and Company, and WILLIAM COCHRANE, both of Glasgow, in the county of Lanark, North Britain, have given notice to proceed in respect of the invention of "Improvements in hot pressing textile fabrics and in the machinery or apparatus employed therefor."
1994. WILLIAM WALTON URQUHART and JOSEPH LINDSAY, both of Dundee, in the county of Forfar, North Britain, Engineers, for an invention of "Improvements in machinery or apparatus for treating or finishing woven fabrics."—Dated 22nd May, 1877.—Notice to proceed has been given.
2261. FERDINAND RATH, of Goldsmith Street, in the city of London, for an invention of "Improvements in machinery or apparatus for plaiting or folding woven or other fabrics."—Dated 9th June, 1877.

THE TEXTILE COLOURIST.

No. 20.]

AUGUST, 1877.

[Vol. IV.

*1. New Colouring Matters Derived from Anthracene.**

BY M. MAURICE PRUDHOMME.

A MIXTURE of glycerine and concentrated sulphuric acid acts in a remarkable manner upon the anthracene series of colouring matters, giving rise to new substances, also endowed with dyeing properties.

I have principally studied alizarine and mono-nitrated alizarine. The alizarine used in the following experiment was the No. 1 of Meister, Lucius, Brüning, and Co.; it is for purple, and is nearly pure alizarine.

A mixture was composed of—

- 1 part alizarine in paste.
- 2 parts white glycerine.
- 2 parts sulphuric acid at 169° Tw.

Upon heating it soon became dark brown, with an abundant evolution of gas and vapours, which contained a little sulphurous acid and acroleine. The temperature should be kept for some time about 200 C. to effect the transformation of the alizarine; it is then allowed to cool, mixed with a large quantity of water, and thrown on a filter.

The greenish yellow product, which remains undissolved

* Bull. de la Soc. Chem., Paris, xxviii., p. 62., July 20th, 1877; communication dated Mulhouse, June 22nd, 1877.

after several treatments with hot water, is put into contact with a cold mixture of equal parts of water and alcohol. This solvent readily separates from it a colouring matter of the alizarine family, but shewing very considerable differences from alizarine.

In dyeing it gives reds and pinks more yellowish, purples bluer, chocolates less red and fuller, and black finer than alizarine yields. Soda, ammonia, and carbonate of soda dissolve it with an orange-red colour, which at once distinguishes it from alizarine, which colours alkaline liquids purple.

If alcohol is added to the alkaline solutions they become dichroic, shewing red by transmitted and green by reflected light, like the salts of chrome. The solution in alum has the same characters as alizarine solution. Its powers of resisting the action of soap, of acids, of chlorine, etc., are the same as alizarine.

The commercial mono-nitroalizarine from the "Anilin and Soda Fabrik" of Mannheim, becomes changed under the same influences, giving birth to some curious colouring matters.

The proportions of materials and treatment were the same as for alizarine.

By treating the washing waters with soda, there was obtained a dark indigo-blue precipitate, which by acting upon with salt of tin and soda, was reduced, giving rise to a pink coloured liquid, which was covered with a greenish blue scum.

The matter remaining on the filter is composed of two distinctly different bodies, easy to separate by cold diluted alcohol.

The substance which dissolves best in this vehicle dyes alumina mordants violet. Strong iron mordants, and mixed iron and alumina mordants, are dyed in a blue-black; weak iron mordants take a very blue grey, similar in shade to indigo.

The other substance gives by dyeing a pretty good black, a greyish lilac, and, instead of red, pink, or chocolate, catechu brown shades having no mixture of red,

This is the first example within our knowledge of any substance dyeing alumina mordants of a brown colour.

Both the colouring matters give colours resisting soap well, less perfectly resisting chlorine, and which are destroyed by strong acids.

Colouring matters are already known of the anthracene series which dye alumina mordants of a purple colour. One is obtained by the action of ammonia in close vessels upon the anthrapurpurine discovered by Perkin in crude alizarine. It appears to be the same as the purpuramide of Stenhouse. The other is a commercial product, made by Gauhe and Co., of Barmen, and does not appear to be of any considerable importance from a practical point of view, for, according to M. Potier's report, the anthraviolet does not dye easily, is irregular, and the colours it yields are not fast to bran, soap, or chlorine.

A stable colouring matter yielding a series of shades similar to logwood, and capable of replacing it in steam colours, yielding faster colours, would at the present day have a considerable value. One of the colouring matters which I obtained from nitroalizarine appears to be close to such a desirable substance.

What is the probable condition of these bodies? It is not likely that they are products of reduction. The members of the alizarine series which are lower than it do not possess any dyeing properties.

They can scarcely be products of oxidation, for the conditions of their origin are nearly the same which lead Lalande to the synthesis of purpurine, and we found no trace of that substance present. We are almost compelled to think that the molecule of glycerine enters directly into the reaction, and that the bodies are glycerides.

I intend to study the same reaction upon different colouring matters such as purpurine, isopurpurine, etc.; of the anthracene series, and also the non-colouring members of the same series, such as anthraquinone and the nitro-anthraquinones.

2. *Ageing or Mastering of Logwood for Dyeing.*

[In the *Muster Zeitung*, No. 29, 1877, from the *Polytech. Notizblatt*, we find some remarks upon this subject which are worth translating. It is known that the dyers who grind or rasp logwood for their own use do not consider it fit for use until it has been wetted and undergone a sort of fermentation accompanied by heating, which takes about six weeks. In the following note the caution against ammoniacal vapours and the use of urine in the wetting, as well as the hastening of the ageing by use of glue or size, are points to be noticed.—*Ed.*]

THE fermentation of rasped logwood is best carried out in the following manner:—For each 100 lb. of the wood, take 30 lb. of clear soft water. The wood is spread out to the thickness of 1 or 2 inches, and degged with the water, say by means of a fine rose degging-can (it is important that this quantity of water should be very uniformly distributed, and the wood equally wetted, or otherwise the fermentation will not be complete); after the degging, the wood is heaped up and well trodden down. After lying in a heap for fourteen days, the wood is spread out again in an even layer, and degged again with 10 lb. of water to each 100 lb. of the original dry wood; this done the wood is again heaped up for eight days, at the end of which time it is ready for the use of the dyer. The following conditions must be observed:—(1.) The wood should be placed in a dark room, where the temperature can be kept from falling too low in cold weather, and with sufficient circulation of air. A cellar with some openings for air is very suitable. (2.) The wood must not be placed in stables recently used, nor near nightsoil, for the ammoniacal gases which are likely to be present do not hasten the preparation of the wood, but actually injure it. For the same reason all mixtures or additions of soda, alkaline ashes, urine, etc., to the degging water, is to be absolutely avoided. Further, the water used should be free

from lime, for it is found that spring water generally is unfavourable to fermentation; the sulphate of lime usually present in spring water is hurtful, and water containing it should not be used. The only good method of hastening the fermentation of logwood is by the use of glue water. For 30 lb. of degging water, 2 lb. of good glue may be used, which must, of course, be dissolved in it before using, and applied to 100 lb. of dry wood in an equable manner; wood so treated can be used after standing two days with perfect success, provided the glue water is applied at a temperature of about 80° F., and the process conducted in a place where the temperature does not fall below 66° F. The idea that the colouring matter is at all increased by the glue is erroneous, it simply acts by setting it free. The desired result can be obtained in a couple of days in this way, which takes three weeks to accomplish by the use of water alone. In using glue for this purpose, care must be taken that it is free from alum or other injurious materials.

3. *On Chrysoline: a New Yellow Colouring Matter Derived from Resorcine.**

BY FREDERIC REVERDIN.

THE colouring matter which forms the subject of this note, and which we have prepared since March of this year at the works of Monnet and Co., Plaine (Geneva), is formed by the simultaneous action of phthalic acid and sulphuric acid upon benzylresorcine.

Benzylresorcine.—This substance is easily obtained either by the action of chloride of benzyl upon resorcine in presence of a small quantity of powdered zinc, or by heating an alkaline alcoholic solution of resorcine with chloride of benzyl, or again by heating in an oil bath to about 300° F., a mixture of 1 molecule of resorcine and 2 molecules of benzyl.

* *Moniteur Scientifique*, August, 1877, p. 860.

The simplest method of making it is to add by degrees chloride of benzyl to resorcine in a state of fusion. There is immediate disengagement of hydrochloric acid in large quantity, and the mass becomes reddish brown. When all the chloride of benzyl has been added, the mass is heated to about 300° F. in a vessel provided with a condenser until the liberation of hydrochloric acid has ceased. The product is then thrown into water, which is raised to the boil in order to expel the remaining traces of chloride of benzyl, the mass is left to settle, and the clear decanted.

The compound thus obtained is in the form of a strongly coloured oil, very thick, insoluble in water, and heavier than it; it distills at a very high temperature, being partially decomposed. It is soluble in alcohol, colouring it yellow, the solution possessing a distinct green fluorescence. Benzyl-resorcine dissolves also with a yellow colour in benzine, chloroform, and ether.

Preparation of Chrysoline.—This colouring matter may be prepared by heating together benzylresorcine and phthalic and sulphuric acids, but it is more economical to employ the following method, which does not require the previous preparation of the benzylresorcine.

In an enamelled iron vessel, heated in an oil bath to 270° or 280° F., place

Sulphuric acid	460 grammes.
Ordinary phthalic acid	1 gramme. (?)

The latter body is transformed by the sulphuric acid, and heat into phthalic anhydride. In the mixture is next placed

Resorcine.....	1 kilogramme.
Sulphuric acid	460 grammes.
Chloride of benzyl	1 kilogramme.

The mass is gently heated in a water; the heat may be withdrawn when the mixture commences to give off hydrochloric acid, and the reaction allowed to continue without heating. When the disengagement of the acid has ceased, which is generally in three or four hours, the reaction may be completed by heating in the oil bath to 280° or 290° F. for

twelve hours; the mass is left to cool, the solid cake is broken or ground, and dissolved in weak caustic soda. It is well to cause it to boil a long time, for there appears to be formation of a small quantity of resorcine ether. When no more of the residue dissolves, the liquid is filtered, and precipitated by hydrochloric acid; the precipitate is washed with cold water, and redissolved in the quantity of carbonate of soda necessary, and then evaporated to dryness. This soda salt of benzylated fluoresceine is the colouring matter, chrysoline.

Chrysoline appears in mass with a green reflection; in powder it has a red-brown colour; it is soluble in water and alkalies; its solutions, which present a fine green fluorescence, are precipitated by acids giving yellow flakes. It furnishes derivatives with iodine, bromine, and nitrogen, all of which are fine colouring matters.

Chrysoline fixes directly upon silk and wool. In dyeing wool it is preferable to mordant it beforehand in a bath of acetate of lead and alum. Cotton is mordanted with sulphate of alumina, and dyed warm.

The shade of chrysoline yellow resembles that of turmeric; it resists light very well.

Yellow colouring matters are also obtained by replacing the chloride of benzyl with the chlorides, bromides, and iodides of the fatty series. Methylresorcine, prepared by heating under pressure resorcinate of soda in alcoholic solution with chloride of methyl, gives also a yellow colouring matter.

4. Upon Silk Printing.*

THE caustic potash is rapidly mixed with gum so that the latter may not form a hard mass, when the gum is dissolved the mixture is strained through a wire sieve and applied with the proper precautions. This discharge gives a buff colour

* Abridged from the work of M. D. Koeppelin upon this subject. *Continued from p. 24, vol. iv.*

upon a blue ground, if this effect is required, the goods are simply washed, dried, and finished.

Blue and White Discharge.—To obtain the discharged places white, the goods after washing are passed into sulphuric acid sours at 4° Tw., and worked in it until the buff colour due to oxide of iron has entirely disappeared and been replaced by white.

Blue Ground with Black, Buff, or White.—One of the steam blacks previously given is printed and steamed, twenty-four hours afterwards the discharge above is printed, and the pieces treated as given above.

We may observe here, that when the discharge is for buff, the pieces are kept twenty-four hours after printing the discharge before washing off, but when the white discharge is required, the pieces must be washed off immediately after they have been printed.

The caustic potash in the discharge composition deprives the blue of its cyanogen ingredients and leaves the iron free, which becomes oxidized and fixes upon the stuff. It is easily understood that the longer the pieces are left exposed to the air after discharging, the greater the oxidation which takes place, and the oxide of iron becomes less soluble in acid, hence the difference in the treatments between the buff and white discharge.

The production of the blue colour by successive operations of mordanting and dyeing is easy to explain. The oxide of iron mixed with oxide of tin is in the first place fixed upon the fibre, which during the dyeing under the influence of the sulphuric acid, forms Prussian blue, the oxide of tin giving it a special purple hue. The sulphuric acid in the dyeing vat contributes to the easy decomposition of the prussiate of potash, and by taking the potash prevents the formation of a kind of soluble Prussian blue, which cannot fix upon the fibre.

Orange discharge upon Blue.

*Steam annatto orange	1 gallon.
Caustic potash at 60° Tw.	1 lb.
Alum	½ lb.

* p. 182, vol. iii.

The potash and alum are lightly heated together to form aluminate of potash, which is added to the colour; if the colour is too thin, gum may be added. After printing, the goods are steamed with the necessary precautions to prevent running of the colour.

Styles derived from the Red Woods.—The kind of red wood referred to is called in French *Sainte-Marthe*, which is similar to the peachwood or sapan wood of the English dyers.

Black Ground with Red Discharge.—We give first the dyeing of the foulards in black, supposing that we are operating upon 230 foulards at once. The goods are twice dipped, washing after each dipping in the following mordant:—

Black Mordant.

Persulphate of iron at 14° Tw.....	12 gallons.
Acetate of alumina at 18° Tw.....	3 gallons.

The goods should be left three quarters of an hour in the mordant at each dipping. After the second washing, the goods are well rinsed, to remove every particle of loose mordant, and then the dyeing can be proceeded with as follows.

Dyeing.—This operation is accomplished at a comparatively low temperature, and by successive absorption of the colouring matter by the silk, so that the mordant may be completely saturated.

In a proper dyeing vessel, about 2½ gallons of red wood extract at 14° Tw. is mixed with from 80 to 100 gallons of water, heated to about 86° F., and the pieces worked in the liquor for half an hour. Then a further quantity of 2 to 2½ gallons of red wood extract are added, the temperature raised to 112° F., and the goods worked for another half hour. Again about 1½ gallons of extract are added, the temperature raised to 130° F., and the dyeing continued for another half hour. The pieces are then washed and slightly soaped at 104° F., washed, dried, and printed with the red discharge.

Red Discharge.

Boiling water.....	2 gallons.
Oxalic acid	2 ½ lb.
Muriate of tin	5 ½ lb.
British gum	8 lb.

This colour is printed, and the goods dried at a moderate heat. The discharge ought to shew its action immediately, and the design appear in crimson on a black ground. The salts in the colour dissolve the iron mordant, and exercise their influence upon the liberated colouring matter, forming with it a crimson lake which adheres to the fibre.

Cleansing.—As soon as the silk is dry, twelve or fourteen handkerchiefs at a time are passed in a capacious vessel containing water, heated to 104° F., to which has been added a small quantity of chalk. The handkerchiefs must be quickly moved about, to prevent the discharge colour marking off upon the black. The use of the chalk is to prevent as much as possible the liability to marking off, by neutralising the excess of acid in the colour at the same time that the thickening is being loosened and dissolved. If there is a beck properly supplied with rollers, it is to be preferred for this operation. The pieces are then washed in running water, and the colours brightened by passing in soap at 112° F. for fifteen minutes; then washed, and passed for a second time in water made slightly alkaline with ammonia. The colours should now have great brilliancy; the goods are finished same as the madder styles.

Resist White, Black Ground, and Red Discharge.—The following resist is first printed :—

Spirits of turpentine	12 oz.
Resin.....	16 oz.
Burgundy pitch.....	24 oz.
Tallow	1 oz.

The materials are heated together in a pot for five minutes and the mixture preserved in well-closed vessels.

The resist is printed in the usual manner, thinning it with spirits of turpentine when it becomes too thick on the sieve cloths.

When the resist is of the proper consistency it gives a good impression, which, when held up to the light, appears quite transparent.

The pieces are then dried; the mordanting, dyeing, and discharge red printing to follow as in the process just given.

Styles Derived from Gall Nuts.—The silk is padded with pernitrate of iron at 30° Tw., and the pieces left in rolls for two hours. Then wash and dye black in decoction of gall-nuts, without the addition of any other colouring matter.

When the black formed by the gall-nuts is sufficiently deep the goods are washed, dried on the tins, and printed with the following colours:—

Scarlet Discharge.

Outline red, No. 1 (p. 124, vol. 2) ...	2 gallons.
Crystals of tin	5 oz.
British gum	1¼ lb.

Yellow Discharge.

Berry liquor at 14° Tw.....	4½ gallons.
White starch	3¾ lb.
Thicken, and while hot add	
Crystals of tin	3¼ lb.
And when cold	
Oxalic acid in powder	1¼ lb.

Green Discharge.

Yellow discharge above	1 gallon.
Sulpho-prussiate of indigo	1 quart.
Extract of indigo	5 oz.
Bichloride of tin	5 oz.

The pieces after printing are treated the same as for the red discharge on black just described.

Buff Styles from Oxide of Iron.—For a plain buff or chamois the silk is padded in persulphate of iron at 70° Tw., and after a while washed; the process again repeated to obtain a sufficient depth of colour; then passed in soap, with addition of one-fourth of its weight of crystals of soda, washed, and dried.

Discharge on Buff.—By printing the scarlet discharge (p. 9) a white is obtained. The oxide of iron is dissolved by the oxalic acid after having been partly deoxidized by the tin salts in the discharge. The pieces must then be washed with care, to avoid marking off. Afterwards any of the common steam colours can be entered in, and a variety of effects obtained.

Styles Derived from Indigo and Nitric Acid.—We may commence by recalling to mind the powerful action which nitric acid has upon indigo, and the effect it has upon animal matters such as silk and wool, which is quite peculiar, in communicating to them a yellow colour without changing their texture in an observable manner, provided the action is not too prolonged, the temperature not too high, or the strength of acid not too great. It is upon the property which nitric acid has of colouring silk yellow that the process of manufacture called mandarining is founded.

This process is well described in the Manual of Thillaye ; but the improvements which were introduced by M. Neron, and our own experience, have enabled us, we believe, to introduce greater regularity into a method which has difficulties which still deter many manufacturers from employing it.

The colour box used for printing the resist for this style is of different construction to the ordinary one, since the resist must be printed while warm. It is made of copper, with a double bottom, into which steam can be introduced. A false colour is put into this box, and is covered with a piece of fine cloth in a state of tension, which serves as the sieve cloth, upon which the warm resist is spread ; or what is more simple, the box is filled at once with the resist proper, and a moveable framework covered with fine calico instead of cloth is kept by means of screws at the level of the melted resist, and serves as the sieve cloth, the resist penetrating through the calico and furnishing the block.

The false colour (or swimmings) mentioned above is composed of 1 part of resin and 2 parts of tallow melted together, and must be kept heated to a temperature of 140° F. in the colour box.

Fatty Resist.

Resin	1 lb.
Tallow	$\frac{3}{4}$ lb.
Yellow wax	2 oz.
Chalk, in powder	2 oz.

When there are blues to be reserved, the quantity of chalk is doubled. When printed the resist is allowed to fix well on the cloth, and to prevent it running or marking off, it is powdered all over with fine sand. When the resist is dry or well fixed, the silk is treated in the following manner, to obtain an orange ground with white design.

Nitric acid at about 40° Tw. is placed in a stone trough provided with two rollers which are made of metal, protected by varnish, and covered with calico; one of the rollers dips in the acid, and the other above acts as a draw roller; the piece passing between the rollers becomes evenly impregnated with the acid; it then proceeds under a guiding roller made of varnished wood, and over a box containing a steam pipe extending the whole length of it, which is equal to the width of the piece of silk being operated upon, and bored with small openings, from which the steam escapes.

This steam meets the silk as it is passing over the box, and causes the nitric acid in it to act upon the material, developing a uniform orange colour upon it, excepting in the parts where the resinous reserve has prevented the acid entering into the fibre.

The silk proceeds directly into a vessel containing chalk and water, where it is led two or three times up and down, and then goes into a large vat of water, from which it is taken to be well washed. At this stage of the operation the printed silk still shows the presence of the resist, and the orange colour has not the degree of intensity which it should have. To raise the colour and to clear off the resist, the pieces are passed for half-an-hour in a bath of boiling soap, which, for 30 foulards, is composed of

Soap	1 lb.
Carbonate of soda	2 oz.

When the colour is sufficiently developed the pieces are washed and dried. The parts printed upon by the resist have not been acted upon by the acid, and remain white, while the ground has acquired a fine orange colour, brilliant and fast.

Before speaking of other kinds of this style, of which there are many varieties, we will first point out the composition of the indigo vat used for dyeing silk blue.

Indigo Vat for Silk.

Water	350 gallons.
Ground indigo.....	42 lb.
Sulphate of iron	195 lb.
Quick-lime	130 lb.
Commercial potash.....	32½ lb.

The sulphate of iron is dissolved in water before mixing, and the lime is previously slacked. When the whole has been well mixed, the vat is stirred up for six consecutive days for a quarter of an hour each day, and then it is ready for use.

We will explain in a few words in what manner it operates. Indigo blue is insoluble in water and in alkalis, but when it is deoxidized and transformed into white indigo it dissolves easily in alkalis. It is, therefore, a deoxidation of the indigo in presence of an alkaline liquid, which has to be accomplished. In the vat above the sulphate of iron is decomposed by the lime, which takes its acid, and its oxide being liberated in contact with the indigo, takes away oxygen from the latter, transforming it into indigo white, which dissolves in the excess of the lime and the potash present. When pieces are dipped into such a vat they become charged with a solution of white indigo, and when taken out and exposed to the air the indigo absorbs the quantity of oxygen necessary to its retransformation into indigo blue, which becomes fixed upon the fibre.

The fatty resists by preventing the tissue of the silk from coming into contact with the solution of indigo produces the same effect as the one indicated in the *mandarining*, and we

obtain white places wherever the resist has been printed and the ground blue.

The dipping of the pieces is made by means of a frame with hooks called a *champagne*, or by means of a vat with rollers. The clearing off of the reserve is done in the same way as in the last style, by means of boiling soap.

We may now enter into the methods of obtaining the various effects resulting from the union of the two operations of mandarining and blue dipping.

Blue Design on Orange Ground.—The cloth is dyed blue on the frame, having the vat well stirred up before entering the pieces; washed and dried cool; then printed with the resist and passed in nitric acid and cleared as before described.

White and Blue Design on Orange Ground.—First print the fatty resist for the white, dye blue, wash and dry. Print the resist upon the blue, and treat with nitric acid, etc.

White on Dark Green Ground.—Print the white resist, and treat with nitric acid, etc.; then, without clearing off the resist and without drying the pieces, dye in the blue vat; wash and clear off in hot soap solution, to take away the resist and raise the shade of the green.

White and Blue Design upon Dark Green Ground.—Print the resist, dye a light shade in the vat, wash, and dry. Print again with resist, put through the nitric acid process, wash, and immediately dye dark blue; wash, and clear in hot soap.

White, Blue, and Orange upon Dark Green.—Print the resist, dye light blue, wash, and dry; print resist to protect the light blue, put through the mandarining process, wash, and dry. Print resist to preserve the orange, and dye strong blue, wash, and soap.

If the nitric acid in the mandarining be mixed with nitrate of iron at about 90° Tw. in various proportions from 25 to 50 per cent. of the acid, according to the shade required, a new series of effects will be produced with a dark ground.

White Design on Chocolate Ground.—Print with the fatty resist; dye blue, and dry. Pad twice over in logwood liquor at 3° Tw. Pass through the nitric acid containing nitrate of

iron, then put the pieces in a vat of water for one hour, so that the iron may react upon the logwood, and then soap.

Blue Design on Chocolate Ground.—Dye blue, wash, and dry. Print on the resist, and pad in logwood. Pass through the nitric acid, and wash as before indicated, and lastly soap.

Blue and White Design on Chocolate Ground.—Print the resist, dye blue, wash, and dry. Print again resist to protect blue, and pad in logwood liquor; pass through the nitric acid, leave in water one hour, and lastly pass in soap and soda.

Orange Discharge on Indigo Blue.—The action of nitric acid is utilised by printing upon the blue dyed stuff a colour composed as follows :—

Discharging Colour.

Water 2 lb.

Starch 2 oz.

Boil, cool, and add.

Nitric acid at 66° Tw..... 3 oz.

After printing, and when the pieces are dry, they are passed over a current of steam as in mandarining; then washed and passed in soap and soda to raise the colour.

Indian Style.—This style consists in a yellow or green ground with a black or red design, and two methods are employed for its production. The first and cheaper method is easy and quick, and resembles the steam styles. The second method, in which indigo and madder replace the red woods and Prussian blue, gives better results as far as regards the fastness of the colours.

First Process—Dyeing in Yellow.—The goods are bleached as for the madder style, then mordanted in alumina as follows:—

Acetate of alumina at 10° Tw. 7½ gallons

Protochloride of tin..... 1¼ lb.

The goods are left in the mordant twelve hours, then washed and dyed either in weld or in quercitron bark, to which a portion of Persian berries is added. For 150 foulards there may be used—

Quercitron extract at 12° Tw.	9 lb.
Berry liquor at 14° Tw.	3 lb.

When the colour has acquired a proper degree of intensity, which takes place in about forty-five minutes at a temperature of 120° F., the goods are washed, dried on the tins, and printed in the following order:—(1) Steam black, (2) Indian red or green; the colours being some of those previously given, then steamed for fifty minutes and washed. It is usual to pass the pieces after washing for five minutes in cold bichromate of potash. This treatment is not indispensable, but it gives a little more solidity to the colours owing to the oxidation of the colouring matter, which is due to the action of the bichromate of potash.

Second Process.—The silks in this process are first printed with the mordants for the madder colours, which are afterwards dyed in the usual way. To preserve the parts intended to be white from the indigo vat and also the reds, they are covered by printing on the fatty resist; the goods are then dyed in the indigo vat, and after clearing and washing are mordanted for yellow and dyed in bark as before, washed, dried, and finished.

The Cochineal Style.—Cochineal with an alumina mordant dyes a brilliant crimson upon silk which resists the action of soap, acids, and light in the same manner as colours derived from madder. The silk is prepared in the same way as for the madder styles, and the following mordant printed on.

Crimson Mordant.

Water	1¾ gallons.
Alum	12 lb.
Dissolve the alum in the water and add	
Acetate of lead	10 lb.

Mix the whole well together until perfect decomposition of the two salts has taken place, allow the sulphate of lead to settle, take 4 lb. of the clear and thicken with 14 oz. powdered gum, and add ½ oz. of crystals of tin. After printing the pieces are hung up to age for forty-eight hours in a warm and

moist room, and afterwards for twenty-four hours in a warm and dry room.

Cleansing of the Mordanted Goods.—In a wooden vat of the capacity of about 20 gallons, dissolve and mix the following:—

Bichromate of potash	12 oz.
Arsenate of potash	4 oz.
Chalk.....	2 lb.
Bran	8 lb.

Heat the liquid to 115° F., and then pass in 35 foulards working them about until the gum is dissolved. The action of the bran, which has been previously described, is augmented by the addition of the other salts which fix upon the stuff all the alumina with which it can combine.

The pieces are then washed, and receive a second passage in bran water alone at 100° F., and washed again.

Dyeing in Cochineal.—In a vat containing about 16 gallons of water, there is placed a freshly-made decoction of 2 lb. of cochineal, to which is added 2 oz. of powdered gall-nuts and 2 lb. of bran. This is sufficient for 35 foulards. The temperature at the commencement should be about 100° F., raised during the first half hour to 130°, in the second to 150°, then to 180°, and even as high as 200° F., if it is required to obtain a good shade, which is ascertained by washing the end of a piece in warm water and forcibly wringing it. A good dyer can tell at a glance with certainty whether the colour is good or not. Afterwards the pieces are washed, passed in boiling bran water, again washed, and finished like madder work.

Black and Crimson.—The outline black and the crimson mordant are printed, the dyeing being the same as for crimsons. When the design requires large masses of black, it is better to print steam black after dyeing and steam, there is less risk of injuring the crimson by this method.

White Resist on Cinnamon Ground, with Crimson, Orange, Black, or Chocolate.—Print the fatty resist or the white resist for black. Pad or print the crimson mordant, age and cleanse as before; dye in cochineal, bran, wash and dry up. The silk now has a crimson ground, white objects, and can

now be printed with steam black or chocolate. Then the following orange colour :—

Orange.

Thick gum water	1 gallon.
Berry liquor at 140° B.....	1 gallon.
Crystals of Tin	2 lb.

Fix by steaming ; wash and finish as the madder styles. The black printed on preserves its forms. The parts printed with orange will be partly pure orange and partly crimson coloured. That is, where the orange has fallen upon the reserved white parts it remains orange, but where it has fallen upon the crimson ground it forms an agreeable chestnut or cinnamon colour.

When logwood is used in the dyeing instead of cochineal, a purple is obtained in the place of the crimson, and printing with annatto, orange or Persian berry, orange analogous effects are produced.

Buff Ground, with Crimson Object.—Print the mordant for crimson, dye in cochineal, pass in bran, and dye in a bath of annatto containing only a small quantity of colouring matter.

[To be continued.]

5. *Upon a New Colouring Matter.*

BY A. W. HOFMANN.*

SOME months ago in communicating to the society a notice upon the composition and structure of chrysoïdin, I pointed out what profits the colour industry might be expected to derive from the labours of Griess, and that the power of fixing amine, amide, and even phenol opened the way to the discovery of an almost endless series of new bodies, and that many of the new compounds thus produced were colouring matters as the aniline yellow (azodiphenyldiamin) of Griess and Martius and the chrysoïdin of Caro and Witt, so that in

* Condensed from *Berichte de Deut. Gessel*, July 23rd, 1877, p. 1,378.

fact a new and apparently boundless field was opened to manufacturers. That this field is being explored with vigour is evident from some researches of which I now make a brief communication to the society.

Some days ago H. Martins, whose friendliness keeps me *au courant* with every thing new which appears in the colour making industry, gave me several uninvestigated dyestuffs which have lately been offered in trade.

One of these substances as I received it was a light red coloured crystalline powder, the hue of which recalled to mind the fiery brilliancy of iodide of mercury; another, distinctly crystalline, possessed a bright violet colour, so that without closely examining it one might have thought it was the peach-bloom coloured chloride of chromium.

The red substance is the soda salt of an organic acid mixed with an inconsiderable quantity of alumina. It dissolves pretty largely in hot water, less freely in hot alcohol, the solution having a deep brownish red colour. The solutions by cooling crystallize with a fine red colour, tending to orange. The salt is insoluble in ether. It withstands a tolerably high temperature without decomposing; at a sufficiently high temperature it swells out strongly, almost like the Pharaoh serpents, and leaves behind a carbonaceous mass extremely difficult to burn.

To isolate the acid the product was dissolved in boiling alcohol, and the solution decomposed by concentrated hydrochloric acid. By cooling the dark violet coloured solution deposited very fine red needles, which retained with tenacity a quantity of mineral matter, and it was only by repeated recrystallizations from alcohol and hydrochloric acid that at length the substance was obtained free from incombustible matters.

The pure colouring matter then shewed as beautiful brown-red needles, which were tolerably easily soluble in water, but still easier dissolved by alcohol, and insoluble in ether. Free alkalis and ammonia dissolve them easily with a brown colour; from these solutions the colouring matter is precipitated in the crystalline form by addition of acid, and the

solution assumes a deep violet colour. The colouring matter contains nitrogen and sulphur. The analysis of the substance dried at 100° C., and controlled by the analysis of the silver and barium salts, agreed with the formula $C_{16} H_{12} N_2 SO_4$.

The interpretation of this analysis and formula was not difficult; there could be no doubt that this was a similarly constituted body to chrysoïdin, and might be built up in several ways, the simplest materials for which appeared to be sulphonaphthalic acid $C_{10} H_8 SO_4$ and diazobenzol $C_6 H_4 N_2$, which together make up the formula of the new body; and in fact experiment soon showed that by the action of diazobenzol upon the alpha-sulphonaphthalic acid the new orange red body was obtained.

The sulphonaphthalic acid was obtained by Schaeffer's method of digesting naphthalin with concentrated sulphuric acid in a water bath; the lead salt next obtained was treated with sulphuretted hydrogen, and the liberated acid after concentration saturated with carbonate of soda. When the solution of this salt was mixed with a solution of nitrate of aniline and nitrite of potash there was immediate formation of dark red precipitate, possessing remarkable tinctorial powers, but still impure.

To purify it it was dissolved in ammonia. A quantity of tarry matter was left behind undissolved. Heated with acid a purer substance was obtained, which, by several crystallizations from a boiling mixture of hydrochloric acid and alcohol, finally yielded the beautiful hair-like needles which were obtained from the commercial article.

6. *Notes from Mulhouse.*

THE Mulhouse Bulletin for July and August, just to hand, contains very little that is new concerning textile colouring. The paucity of matter offering has led the editors, contrary to their usual practice, to insert previously published papers, and

we find in this number the article upon Chlorate of Chromium, by Depierre and Tatarinoff, which first appeared in this journal (April, 1877). It is followed by a report written by M. Albert Scheurer, but the reporter has nothing to correct, and nothing of any value to add on the subject. As an historical matter, we may give the contents of a sealed note deposited in 1855 by M. E. Mathieu-Plessy, and opened in 1876. It refers to a proposed plan of obtaining an olive green from chromium salts along with dyed work.

"It is well known," says the writer, "that the number of colours which can be printed at the same time as the mordants of alumina and iron to be dyed in madder is very limited." The author has succeeded, after many trials, in combining an olive from chromium with these colours. It is prepared as follows:—

Bichromate of potash	4 lb.
Arsenious acid	3 lb. 15 oz.
Sulphuric acid at 169° Tw.	3 lb. 3 oz.
Water	8 lb.

"These quantities will yield one gallon of liquid which, without any thickening, is to be printed upon calico which has been previously padded in a solution of acetate of potash at 14° Tw. The black which is to be printed at the same time as this colour is rather different to the ordinary black. The red and other colours are the same as usual." The black is composed as follows:—

Acetate of iron	1¼ gallons.
Arsenite of soda containing 5 lbs. arsenic per gallon	3 lb.
Pyroligneous acid	3 lb.
British gum.....	15 lb.
Tar	3 lb.

"After printing age for three or four days, fix in a bath at 122° F., containing two per cent. of caustic ammonia and one per cent. of silicate of soda. Dye in garancine, not going to a higher temperature than 122° F.; clear as usual. The chief points of difficulty encountered by the author in the process were (1st) obtaining the green dark enough, (2nd) to

prevent acting upon the black and red, where the green touched these colours, and (3rd) to find a suitable fixing liquor."

Several other sealed packets of old date were opened, some of which are announced for publication, while others were deposited in the archives of the Society.

7. *Note upon the Treatment and Dyeing of Textile Matters.**

BY E. DURWELL.

Of Textile Matters in General.—Textile material is the term understood for all substances, animal or vegetable, which can be spun and woven so as to give a thread or a cloth sufficiently consistent for the purposes it is intended to fulfil. The number of textile substances is very great. From the spinner's and weaver's point of view, all these bodies resemble each other except in the matter of the mechanical treatments necessary. From a chemical point of view it is quite otherwise. The composition of many of these bodies varies considerably, and their properties are different.

The three types of textile materials are, *wool, silk, and cotton*. There are others which resemble these three in composition, which may be classified as follows :—

Wool.	Silk.	Cotton.
Hair.	Wild silk.	Flax.
		Hemp.

We shall only treat of the matters named above, for they are the only ones which have a considerable use in manufactures.

* From the *Moniteur de la Teinture*, June 5th and 12th, 1877, taken from the *Bulletin de la Société Chimique*, according to a foot note which does not give any further reference. The matter is superficial, and not always accurate; but from some points it is interesting, and we have thought it worth translating and insertion in the *Textile Colourist*.—*Ed.*

In dyeing the textile materials have four principal treatments, (1) preliminary treatment, (2) bleaching, (3) dyeing, (4) finishing. The preliminary treatment consists in removing from the textile matters other foreign matters not useable as textiles. This usually precedes the spinning and weaving.

The bleaching takes place only after spinning or weaving. Its aim is to remove all impurities which may have been introduced into the fibres during their mechanical treatment, and to clear out those which were not removed by the preliminary treatment.

The dyeing follows the bleaching. This operation consists in fixing upon the yarn or cloth one or more colouring matters, so as to obtain the colour, hue, and fastness of colour desired. Fibres may be dyed in the wool or in the piece, that is, either before or after weaving.

The finishing consists in fixing substances upon the yarn or cloth which give brilliance and consistency.

Of Wool and Hair.—Wool as it comes from the animal is a nitrogenized organic matter, containing a small quantity of sulphur. It is covered with an obnoxious greasy matter called the yolk (*suint*). This substance is almost completely oxidized, or, to speak more explicitly, it is in a rancid state. Other hairs, such as goats' hair, camels' hair, etc., have a similar composition, but do not contain so much yolk as sheeps' wool.

All the processes used to separate the yolk from the wool are based upon the saponification of the greasy matters in it. The wool is treated by soda and washed. The fatty matter removed is utilized by converting it into a lime soap. The wool may be in the first instance treated with oil, the saponification is then more complete. The yolk being oxidized as it issues from the pores of the animal, and especially after long contact with the air in the fleece, I endeavoured to deoxidize it by means of nascent hydrogen. With wool so treated the saponification was very perfectly accomplished. In order to destroy foreign matters contained in the wool such as burrs, thistles, or straw, it is steeped in dilute sulphuric acid and gently heated; the vegetable matter

becomes carbonized, but the wool is always a little acted upon.

Bleaching of Wool.—Before dyeing wool must be bleached either woven or unwoven. For unspun wool the fleece is placed in a bath of boiling soap and water, washed and finished by a treatment with dilute sulphuric acid.

Woven woollens are caused to pass under wooden rollers plunged in a bath of boiling soap, being careful to avoid creases and folds, which would cause injuries after drying, rendering the piece unsaleable.

After soaping, the piece is drawn through clean water, and then receives a weak brightening treatment.

The permanganate of potash treatment is quite satisfactory, but demands much care. The cloth is passed in a bath of water containing 1 lb. of permanganate to 2 gallons of water; when all the permanganate necessary to oxidize the impurities is reduced to peroxide of manganese the cloth is passed into a boiling bath composed of

Water	100 parts.
Bisulphite of soda	8 parts.
Hydrochloric acid	4 parts.

The cloth being thus bleached is washed in boiling water; in rare cases it may be necessary to repeat that operation.

In the treatment of woollen goods all copper utensils must be avoided; they are nearly always the cause of disagreeable accidents. In employing the apparatus known as an "extender," in which the piece passes over copper rollers immersed in boiling soap, I have invariably observed, notwithstanding the perfect cleanness of the apparatus, stains and brown patches due to the combination of the copper and the sulphur of the wool favoured by the alkaline liquid. To recognise these copper stains it is sufficient to pass the cloth into a solution of chloride of tin; if the stain be owing to copper, it will assume the colour of metallic copper.

To remove these copper stains from wool I pass the pieces in a boiling bath containing 100 parts of cyanide of potassium for 2,500 parts of water, brighten, and wash.

Dyeing of Wool.—It is not our aim to describe particular

processes as employed in this or that dyeworks, but to give a general idea of wool dyeing.

Wool is dyed at boiling heat. Several authors have supposed that the greater or less aptitude which textile matters have for taking or retaining colouring matters depends upon the numbers, size, and distribution of the pores, and their proportions with the colouring particles.

In strongly aluming, 500 parts of wool and 500 parts of silk, it is found that to obtain the same intensity of colour by dyeing it is necessary to take—

For 500 parts of silk, 76 parts of cochineal.

For 500 parts of wool, 30 parts of cochineal.

As regards mordants, wool and silk are similar, with the single difference that wool is dyed very hot and silk cool, when the latter is mordanted (G. van Laer.) Cotton dyes in the cold, evidently because its pores are smaller. But the mordant aside, the question should be considered in another manner, for there is, besides cohesion, another cause; there is frequently chemical affinity, especially with the coal-tar colours. Often, however, a mordant is required. In that case it is not the textile fibre which acts, it is the mordant. The fibre acts only as a ground, it is the mordant which combines with the colouring matter.

Wool and woolly hair when it is bleached is ready for dyeing.

To dye wool with the salts of the bases derived from coal-tar it is necessary to use the bath boiling, and in an acid condition with salts of rosaniline, salts of violaniline, soluble blues, etc. It is necessary that the colouring matter, which is the salt of the base, and not the base, should reform within the pores of the wool. The iodine green which is decomposed by contact with acid cannot be used with an acidulated bath. For this colour it suffices to employ a neutral salt of one of the alkaline earths, such as sulphate of magnesia, and to dye at the boil. This salt yields up a part of its acid to the wool, and the dyeing may be successfully accomplished.

The wood extracts should not be added to an acid bath

unless it is desired to obtain some distinct effect. Wool has the property of absorbing all their colouring matters without the intervention of other substances. It is well known that wool absorbs very easily catechu, and generally all varieties of tannin matters.

In piece dyeing the smallest quantity of colouring matter possible must be employed, and the liquid maintained at the boiling heat to avoid stains. The baths should be kept clean, especially for light shades, for wool has a powerful tendency to combine with mineral salts, especially in the presence of acid; this is easily proved by placing acidulated wool in contact with copper, iron, bismuth, etc., or with salts of these metals. Wool dyeing must as much as possible be carried out in wood vats at the bottoms of which the steam pipes of tinned copper are placed. Copper dye vessels so much used should be rejected.

Other hairs are dyed exactly in the same way, taking precautions when they are in the fleece against felting and curling.

Silk and Wild Silk.—The silk contained in the *phaelena bombyx* is liquid and gummy; it hardens as it is forced out by the animal, and allows a yellow, waxy matter to exude which covers the fibre like a varnish. The substance composing the solidified silk is called fibroin (Pelouze and Frémy). The waxy matter is called the gum.

The fibroin is soluble in hydrochloric acid, phosphoric acid, and very concentrated hyponitric acid, and also in cupro-ammonium liquor; it appears to be a true organic base.

By acidulating water with about 1 per cent. of the sulphuric acid, and adding a certain quantity of litmus the liquid is distinctly red. Let a quantity of silk be purified by washing the already boiled off and bleached silk with boiling alcohol and boiling distilled water, it will be found that in this state the silk always shews an alkaline reaction, turning the red litmus to blue.

By heating the silk in the litmus solution the colouring matter is absorbed, and the silk is not dyed red but blue; the acid has evidently been neutralized by the silk. The dyeing

stops when all the acid has been absorbed and the excess of litmus left in the liquor changes to blue, it having become neutral. By treating the dyed silk with boiling water containing about 1 per cent. of caustic soda it is immediately decolourized. By dyeing a further quantity of purified silk in a 1 per cent. solution of neutral sulphate of magnesia containing neutral litmus and boiling it, the litmus is absorbed and the liquor remains blue.

Fibroin dissolves in concentrated hydrochloric acid, and the solution left to evaporate spontaneously in the air becomes of a syrupy consistence. This matter when treated by boiling alcohol and evaporated leaves a horny, semi-transparent substance, nearly neutral, which is a combination of the hydrochloric acid with the silk. It has the property of absorbing the coal-tar colouring matters the same as silk passed in an acid solution of the same colours. I go no further than setting forth these two conclusive experiments, and do not attempt to draw from them any theory, for any hypothesis deduced would be on too small a basis. But it seems proved that the presence of an acid is nearly always necessary in silk dyeing.

Treatment of Silk before Dyeing.—To prepare silk for dyeing the gummy matters must be removed. To effect this the silk is treated in a boiling bath of 25 parts of soap to 100 of water, and kept in it for several hours; the soap is then found to be completely decomposed, it loses its syrupy consistence and its property of frothing, while a part of the oil floats above.

It would be decidedly preferable to pass a boiling solution of soap through the silk properly packed in an aspirator. On the small scale this plan succeeds, and with a saving in soap.

Silken tissues are submitted to the same operation with the only difference that they are suspended from wooden frames and dipped in the bath of boiling soap. In either state the silk is afterwards washed and finished. For whites and for receiving fine colours the bleaching is finished by a passage in the sulphuring stove. Sulphuric acid often forms in the sulphuring chambers owing to an excessive degree of humidity

and exposure to air; these two defects must therefore be avoided.

The process of bleaching by means of bisulphite of soda is very expeditious, but the results are not so good. A bath may be prepared with

10 parts bisulphite of soda.
6 parts hydrochloric acid.
100 parts water.

The bath is used slightly heated, and the silk passed through it.

Dyeing.—Silk dyeing is the same as wool dyeing. Woods take at the boil either with or without presence of acid.

Silk possesses in a very high degree the property of absorbing tannin, and it is in consequence one of the materials used for *weighting* silk.

The salts of the coal-tar bases dye in a boiling acidulated bath, but Magdala pink and iodine green do not require any acid.

Wild silk, which is coming more into use every day, has the property of being soluble in alkalies. In making some dyeing experiments with cloth of wild silk I used safflower in boiling soap solution, but the cloth fell to pieces, I might almost say it dissolved.

The dyeing of wild silk is the same as that of ordinary silk; it does not, however, yield colours so good.

Of Cotton, Flax, and Hemp.—Cotton is nearly pure cellulose; the other vegetable fibres, after retting and bleaching, are nothing but cellulose, of which the fibres are more compressed than those of cotton; they have therefore the same chemical properties, but their dyeing is more difficult on account of their smaller degree of porousness.

The question of the *animalisation of cotton*, which some years ago went the round of all dyeworks, is a Utopia. To convert cotton into silk is just as impossible as for a chemist to make a grain of wheat out of phosphate of lime, starch, and gluten. Silk will never be made except with silk. By putting a solution of silk upon cotton, as in Muller's patent, there is no animalisation of it. By putting albu-

men, caseine, gelatine, or tannin, or mixtures of these substances upon cotton, the cotton is mordanted and nothing more. It has been shewn lately that gun cotton can absorb the colouring matters of the coal-tar class, but it does not follow that because a non-azotised substance transformed into an azotised one possesses some properties which belong to silk that therefore it should have all its other properties. I conclude by saying that cotton requires a mordant, if even silk be dissolved and fixed upon cotton, or any other body, it is always as a mordant. There are some substances absorbed by cotton without the intervention of a mordant as, for example, catechu, phosphine, a yellow colouring matter derived from coal-tar, and several other yellow and brown colours of the same class.

By passing cotton through a bath composed of dextrine mixed with Hoffmann's purple, or with fuchsine, it becomes immediately dyed. Does the dextrine here act as a mordant or as a thickening?

Tannin is the true mordant for the aniline colours upon cotton. It precipitates them all, and it is that property which gives it its power of mordanting, in addition to which it fixes itself very easily upon cotton.

Mixed Silk and Cotton Goods.—I will speak briefly of cotton and silk mixtures, which have become the object of an extensive branch of dyeing.

At first the question seems very simple to dye cotton and silk at the same time, but I have already shewn that these two fibres are chemically distinct substances, and possess different properties.

The goods are first singed by passing over cast-iron cylinders heated to a cherry red heat. They are afterwards cleansed in a bath of boiling soap, in the same way as silk goods.

The soluble blue and Hoffmann's purple are the two coal-tar colours which are the most unequally absorbed by cotton and silk. Sometimes the silk is too light, and sometimes the cotton, more generally the cotton. If a piece of the mixed fibres be placed in a cold bath of soluble blue, the silk

absorbs the colouring matter while the cotton remains untouched. If again another piece be first treated by a bath of tannin and then by a bath of gelatine, the gelatine becomes precipitated and fixed. By passing such a treated cloth into soluble blue, both fibres take the colour equally. In this case the cotton is mordanted.

Soluble blues are generally fixed upon these mixed tissues as follows:—The cloth is passed into a bath containing 2 parts of tannin to 100 parts of water in the cold; next pass into the blue containing a little tannin. The cotton will be found to have absorbed the colouring matter in the same degree as the silk. It is necessary not to have more than a small quantity of blue in the dyebath at one time. To dye the Hoffmann purple the tissue is passed in a very strong solution of tannin, which, by refreshing with tannin every time it is used, may serve for several operations, and afterwards into a very weak bath of the colouring matter. The piece must be worked for a long time in the liquor to obtain a satisfactory result. With this precaution, and by well mordanting the cloth, the cotton can be dyed a dark shade. It is seen that while tannin has the property of mordanting the cotton, it deprives the silk of its power of absorbing colouring matters, as may be proved by the following experiment. Pass the mixed tissue in a cold concentrated bath of tannin made with 100 parts water and 30 parts tannin; afterwards pass into pyrolignite of iron, and lastly into a bath of logwood and chestnut bark; the cotton takes an intense black, while the silk has only become yellowish. In the goods called "Chinas," where the silk is in mixture with the cotton, after dyeing the black as above, the silk being lighter than the cotton, communicates to it a lustre which makes the cloth more brilliant than otherwise it would be. For other goods a piece dyed black as above, can be passed into a coal-tar colour, and the silk dyed a bright colour, the black cotton beneath giving it a rich appearance. To dye these goods with iodine green, they are mordanted in sumach or in tannin, and passed into a cold bath of the colouring matter, to which some tannin is added.

Fuchsine or magenta fixes in the cold upon a tannin mordant. The dyeing must be always done cold, and the smallest possible amount of colouring matter added.

Blacks upon these mixed silk goods are well dyed by mordanting in pyrolignite of iron, well washing and dyeing as for cotton, avoiding always a too great excess of tannin matters, which injure the silk, and observing that the dyeing must be done cold.

The steaming of these goods give very good results. The cotton becomes darker and the silk becomes more brilliant; the greens become bluer instead of yellower as is the case by dry heat; with the soluble blues the cotton becomes redder and the silk greener.

This sketch, as it will have been observed, is very incomplete, it is not a treatise upon dyeing. I have endeavoured in this collection of notes to connect together in a practical manner the various textile materials, and trust to be able at another time to enlarge upon this interesting branch of the applied sciences, dyeing.

8. *New Work on the Sizing of Cotton Goods.**

THIS work from the pen of Mr. Thomson is, we learn from the preface, an amplification of a lecture he delivered recently at the Society of Arts, London. The textile colourist is in general little concerned with warp sizing, which is for him only a subordinate operation in the weaving of calico, but there are occasions when it becomes a point of vital interest to the bleacher, dyer, and printer, to know what has been used in the operation of sizing, for it sometimes happens that defects in colour can only be attributed to an imperfect removal of the sizing from the cloth dyed or printed; this may

* "The Sizing of Cotton Goods, and the Causes and Prevention of Mildew." By Wm. Thomson, F.R.S., Edin., F.C.S., Lond. Manchester, Palmer and Howe; London, Simpkin, Marshall, & Co.

be the fault of the bleacher, who has not used proper means of cleansing the cloth, or it may be the fault of the sizer, who has employed ingredients in the size which ordinary bleaching will not take out. It is not within our province, in this journal, to treat of sizing further than it concerns the after operations to which the sized cloth is submitted in the operations of bleaching and dyeing, and we are happy not to have to consider the "moral bearings," as Mr. Thomson has it, of sizing to give weight. The simplest and most innocent size gives difficulty enough to the bleacher, and requires him to prolong his boilings hours upon hours to thoroughly remove it from the warp threads, none of it is left in the bleached cloth (or none of it should be left in) which is used for printing or dyeing. To size cloth intended for such purposes with the intention of increasing its weight and improving its feel temporarily, may have "moral" or "immoral bearings," that is a question, but there is no doubt that there is something like hopeless imbecility on the side of either the maker or the buyer of such weighted cloth. On page 195 Mr. Thomson refers to the use of paraffin wax in sizing, and shews that it and similar substances ought not be used for sizing cloth for dyeing or printing. In the pages of this journal it has been shewn that the use of unsaponifiable waxy matters has led to inconvenience and that it probably would again. Some manufacturers consider that the use of paraffin wax instead of tallow in the size gives considerable advantage, there is no economy in price, and it is only used because better cloth can be made by its means. It is said also that scores of thousands of pieces made from warp sized with size containing paraffin wax have been printed and dyed without complaint, this is doubtless so, but as M. Ch. Benner has shewn with regard to Japan wax (*Textile Colourist*, i., p. 102), there is always a danger of damage arising from the use of such substances. It must not be forgotten that neither tallow nor wax dissolve in the hot size, they are only in a finely divided state, and with regard to either, and especially to waxes of a comparatively high melting point, they may easily separate from the size by standing or by

cooling, or some such accident, and particles get upon the threads, which are then melted in by the drying, and so fixed that common bleaching will not take the matter out. In a given case 1 lb. of paraffin wax is spread over 330 lb. of calico, if it is perfectly evenly spread, it is difficult to suppose it would be found injurious to any colours. It is in being unevenly spread that the danger exists. Mr. Thomson's work goes into very minute detail upon all the materials used in sizing, and the apparatus necessary for the proper chemical examination and testing of them. It will certainly prove useful and valuable to a great number of merchants and manufacturers engaged in the cotton trade.

Testing Flavine for Turmeric.—In a recent number of the *Färber Zeitung* Dr. Reimann states that flavine has been found fraudulently mixed with turmeric, which has considerably less value in the market. The detection of this adulteration is not difficult, since flavine dyes only upon a mordant and turmeric is one of the so-called substantive colours which does not require a mordant. To test for turmeric in flavine it is therefore sufficient to make a hot solution of the suspected matter and introduce into it some unmordanted cotton yarn. If turmeric be present the yarn is soon dyed of a characteristic yellow colour, quite different in shade and intensity from the faint colour which such cotton takes from unmixed flavine.

9. *Abridgments of Complete Specifications of Patents Recently Published.*

A.D. 1876, November 25th.—No. 4577.

LAKE, WILLIAM ROBERT. "Improvements in the Application of Certain Salts and Soaps for the Preparation of Threads and Fabrics to give them Stiffness, Render them Impermeable, and Improve their Appearance." (*A communication from Claude Garnier, of Lyons, France.*)

"This invention relates to the preparation of threads and

fabrics of various kinds and of any shades or color in such a manner as to give them stiffness and impermeability, and an appearance superior to that presented in their primitive or natural condition, by swelling or thickening their fibres. For this purpose I employ various salts and soaps, as hereinafter described.

"The salts and soaps which are preferably employed in practising this invention are the following, namely, the alkaline bistearates, alkaline bioléates, alkaline bimargarates, alkaline bipalmitates, and alkaline biresinates, and the neutral metallic salts of the aforesaid various acids and formed by alumina, magnesia, zinc, lead, and the like, that is to say, uncolored metallic salts soluble in different vehicles, or which can be formed on fibre by double decomposition by means of two preparatory baths.

"The alkaline bisalts are very translucent, insoluble in water, easily soluble in benzine, essential oils, alchols, sulphide of carbon, and the like; consequently they are easily applicable to threads or fabrics by the ordinary manipulation. They give all the desirable rigidity when employed in sufficient quantity; they also render the material sufficiently impermeable to prevent the soiling or spotting of the fabric by rain; being translucent they do not injure the most delicate colors; and not being fusible, except in a temperature above 100° centigrade, they do not become softened by the heat of the sun, and the fabrics which are impregnated with them are dustproof. They have thus imparted to them all the desired qualities for an excellent impermeable preparation.

"The ammoniacal bisalts are generally very easy to prepare; do not reduce the colors like free fatty acids, and it is these that are employed most frequently for silk fabrics, principally for taffetas, serges, handkerchiefs, and the like.

"I would also observe that neutral ammoniacal salts which are soluble in water are easily transformable by heat in insoluble bisalts. In many cases I may employ an aqueous solution of these neutral salts, which by the ordinary preparation will give the required bisalt. This solution is employed especially for light dressing, with the object of thickening the

fibre, without producing great stiffness or impermeability, and for what is termed false dressing.

“For stronger dressings it is necessary to dissolve the bisalts in benzine, essential oil, sulphide of carbon, alcohol, and the like, in such a manner as to fix the product more effectually on the thread or fabric. The quantity employed varies according to circumstances, and depends more especially upon, first, the results desired to be obtained, that is to say, the strength and quality of the dressing; second, the nature of the salt employed for this dressing or preparation; third, the quality and nature of the stuff; fourth, the color of the said stuff. For black taffetas and the like I usually employ in dry bistearate of ammonia from 60 oz. to 250 oz. for each quart of the dressing. For colored stuffs, especially those with clear colors or shades, the quantity is less, and is reduced to about 12 oz. to 90 oz. per quart.

“I may mix divers of the above-named salts and apply them together for obtaining a dressing or preparation of any determined quality.

“In some instances, especially with regard to impermeability and principally with black stuffs, I may employ the following, namely, paraffine, spermacetti, vegetable, or Japanese wax, mineral or fossil wax, or the like, dissolved in benzine or other suitable solvent. In this case I seek for substances having a high fusion point, to avoid the settling of dust which would result from softening by the heat of the sun; these substances are specially applicable to black silk stuffs and similar materials.

“For colored stuffs I prefer to employ almost exclusively those bisalts above specified, which alone permit of obtaining results not hitherto produced.

“For rendering the material impermeable and giving a suitable stiffness thereto by means of metallic soaps, such as the oleates and stearates of alumina, I proceed either by means of a single bath with a suitable solution of soap in an appropriate vehicle, or by forming these salts on the stuff by double decomposition by means of two baths. The first is given with a solution of bistearate of ammonia, for example,

in benzine, and the second with an aqueous solution of acetate of alumina ; the latter can be obtained by pulverization.

"I can also render the material sufficiently impermeable to prevent soiling by rain, especially for silk handkerchiefs, silk and woollen stuffs, and silk and cotton stuffs, by the following treatment, that is to say, I provide a preparatory bath of a suitable consistency with *hai-thuo* or gelose, *fucus crispus*, *algæ* of various kinds, and lichens, and I add to these a concentrated solution of pure acetate of alumina. In this case the drying in the air or airing, the passage of the stuff to the heated drums, and the action of the vegetable acids, *fucus*, *algæ*, or lichens will expel the acetic acid of the acetate, so as to produce insoluble sub-salts of alumina, which do not easily become wet or moist, and thus form preparations of sufficient impermeability.

"I may also employ gum and glue mixed with acetate of alumina, but in this case the results obtained by the free alumina or by the sub-acetates are not so perfect, and it is preferable to use the above-named vegetable substances containing natural organic acids, such as lichen, stearic and pectic acids, and the like, or acids formed by modification of the pectic products of these substances, as then the acetic acid of the acetate can be expelled more easily by heat in obtaining insoluble salts of alumina.

"Having thus fully described the said invention, as communicated to me by my foreign correspondent, and the manner of performing the same, I wish it understood that I claim the employment of the above specified various salts or soaps for giving to threads and textile fabrics of all kinds and of all shades or colors stiffness and impermeability, and an appearance superior to that presented by them in their primitive or natural condition, by swelling or thickening the fibres, while at the same time ensuring a permanent effect of the dyeing, as above set forth."

A.D. 1876, November 27th.—No. 4580.

ALEXANDER, EDWIN POWLEY. "Improvements in Apparatus or Means to be employed in the Treatment of Woolen,

Silk, and Mixed Fabrics or Goods with a View to the Destruction of any Vegetable Fibres or Substances contained therein." *A communication from Daniel Michel, of Paris. (This invention received provisional protection only.)*

"This invention relates to further improvements in the invention for which Letters Patent were granted to me on or about the 25th of November, 1875, No. 4088, and also on the invention for which I obtained provisional protection on or about the 17th of July last, No. 2916, and consists of a peculiar construction and arrangement of apparatus to be employed in effecting the destruction by carbonization of any vegetable matter that may be contained in woollen or silk goods or waste, or in mixed fabrics or rags containing cotton warp or weft.

"In carrying out this invention a closed chamber is employed, the interior of which is raised to an elevated temperature by steam pipes or heating flues, and within which chamber gaseous hydrochloric acid is disengaged by the action of the heat from the before-mentioned steam pipes or heating flues or vessels containing hydrochloric acid situate in the bottom of the said chamber. The interior of this chamber from the top downwards is furnished with a series of endless wire gauze aprons travelling over horizontal rollers disposed in vertical rows, and made adjustable vertically to accommodate layers of material of different thickness upon the wire gauze aprons. The said rollers are driven the one from the other by spur or other gearing, so as to cause the materials under treatment to travel to and fro across the chamber, dropping from one apron to the other from the top downwards until they finally issue through an aperture in the side wall near the bottom. A similar aperture at the top admits the fresh material, the top and bottom aprons being extended outwards some distance beyond the chamber to facilitate the charging and discharging of the entering and delivering aprons. A pressing roller is situate above these two aprons just outside the chamber so as to partially close the apertures and check any escape of gas, whilst at the same time compressing slightly the materials.

"Wooden doors lined with lead are provided at the lower part of the chamber for the introduction and withdrawal of the vessels containing the hydrochloric acid."

A.D. 1876, November 29th.—No. 4625.

ASHWELL, JOHN ROGERS. "An Improvement in the Process of Dyeing Hosiery Goods."

"Hitherto in the dyeing of cotton and merino hosiery goods with indigo in an ordinary blue vat it has been found impossible to secure an even tint. This is due to the rapid action of the air on the color so soon as the goods are exposed to its oxidizing action on their removal from the vat, the outer surfaces becoming dark during the process of wringing out the excess of dye liquor, and there ensues a streaky and uneven color consequent upon irregular expression of the dye liquor.

"To provide against this unsatisfactory result, which is given both by hand wringing and when the goods are submitted to the centrifugal wringer, I propose to proceed in the following manner:—Supposing it to be required to dye stockings or any other hosiery fabric I submit the goods to the dye liquor within a cage."

This cage is figured in a drawing accompanying the full specification. It is sufficiently described in the provisional specification as "having a closed wooden or iron bottom, with solid sides, the upper portion of which are perforated so as to allow free penetration of the liquor from the vat into the cage." The complete specification then proceeds:—

"The use of this construction of cage prevents the agitation of the goods within the cage from stirring up the deposit at the bottom of the vat and so coming in contact with the goods and acting injuriously upon them. By placing the cage charged with hosiery goods in the blue vat the goods will be immersed in the liquor; here they are subjected to agitation as usual to ensure the penetration at such a distance down as will shut off the deposit from the supernatant liquor, such partition having doors which can be closed when the vat

is in use. When submitted for a suitable time to the dye liquor the stockings or other articles of hosiery are to be fished up and placed in the bite of a pair of adjacent elastic squeezing rollers. Rotary motion being given to these rollers the surplus dye liquor will be rapidly and evenly removed from the goods before exposure to the action of the air; thus the goods will be free from inequality of tint, and by a repetition of the dyeing and squeezing process an even colour of any desired depth will be obtained.

“When it is more convenient to perform the wringing operation at some distance from the blue vat the goods are removed from the vat in detached quantities in a vessel charged with dye liquor from the vat. In this case also they are submitted to the elastic squeezing rollers in such manner as will avoid their unequal exposure to the oxidizing action of the air.

“The mode of carrying out the improved process of dyeing hosiery goods I will now proceed to explain in detail:—As a preparation for dyeing, the goods are scoured or thoroughly wetted, and they are then passed through the hydro-extractor. While yet wet, they are straightened out and taken to the vat, where the cage being already lowered into the indigo dye liquor the goods are immersed within the same and stirred up until the penetration of the dye is complete; this will take in general about ten minutes. The goods are then removed. By preference I quickly transfer them to a small box held to the edge of the vat and containing dye liquor sufficient to cover them. While thus submerged they are carried and placed in the nip of the squeezing rollers; or the box may be lowered into the cage and the goods placed therein with a dyer's stick under the surface of the dye liquor. The box thus charged is carried to the rollers where the goods are fished out one by one by hand and passed between the elastic rollers to squeeze out the surplus dye liquor. After this operation the goods are exposed to the air. They may then be rinsed in water, ‘soured,’ *i.e.*, dipped in weak acid, again rinsed with water and dried. If required the goods may be scoured before being ‘finished.’

"The process from immersion in dye liquor to exposure to air is repeated in this order until the desired depth of tint is obtained. In preparing the dye liquor, from one-tenth of a pound to 0.150 lb. of indigo will be used to each gallon of water employed.

"Having now set forth the nature of my invention of 'An Improvement in the Process of Dyeing Hosiery Goods,' and explained the manner of carrying the same into effect, I wish it to be understood that under the above in part recited Letters Patent I claim in dyeing hosiery goods with indigo, the treatment of the same in and on their leaving the dye vat in the manner above described, whereby I am enabled to ensure an even blue tint in the goods."

A.D. 1876, December 1st.—No. 4654.

BUTLER, JOHN SWINTON. "An Improved Process for Treating Vegetable Fibres."

"My invention consists in an improved process of treating vegetable textile fibres (such as cotton, flax, jute, hemp, and China grass), whereby these fibres undergo a change in their nature and appearance, and acquire the characteristic qualities of silk, for which they are adopted to be used as a substitute.

"My improved process is as follows:—

"The cotton or other fibres to be operated on (hereafter referred to as the fibre) having been first freed from its starchy, fatty, and gummy matters by any suitable known means (for example, by immersion in chlorine water for about eight hours) is thus treated:—

"First. The fibre in a moist condition as it comes from the preliminary treatment above referred to is steeped for twenty seconds in monohydrated nitric acid, specific gravity 1.520, and then quickly washed and rinsed in an abundant supply of running water until it is perfectly neutral to test paper. Care must be taken to avoid the conversion of the cellulose of the fibre into pyroxline or gun cotton by limiting the immersion in nitric acid to the time indicated (which may, however, vary according to the strength of the acid) and by carrying out the operation as rapidly as possible.

“Secondly. The fibre is then immersed for about fifteen minutes in a solution of sulphite of soda, in the proportion of about $2\frac{1}{2}$ per cent. of the weight of the fibre, and a strong galvanic current is passed into the bath to decompose the sulphite of soda. The galvanic current should be produced by a Ruhmkorff’s coil capable, with six large Bunsen battery cells, of producing a spark two or three inches long. The vessel in which this part of the operation is conducted may be of copper or any other suitable material, and the temperature of the bath should be about 100° Fahrenheit.

“Thirdly. The fibre is then boiled for about half an hour in water containing about $1\frac{1}{2}$ per cent. (by weight) of carbonate of ammonia and afterwards washed in pure water, and when clean and colorless the fibre is treated with an ammoniacal or acetic solution of natural raw silk, or it might be manufactured silk undyed (in the proportion of about one-half part to one hundred parts of fibre in sufficient water to cover the fibre) in a vessel of tinned copper, and under a pressure of four or five atmospheres and at a corresponding temperature, the galvanic current being at same time passed through the material by connecting the poles of the coil with the exterior of the vessel containing the fibre and silk solution. The passage of the galvanic current is continued until the liquid becomes milky or gelatinous. The fibre, which at this stage acquires the appearance and character of silk, is then placed in a drying room, and when dry is washed and rinsed, and finally dried again. The product will then be nearly white or colorless, and may be prepared for dyeing in the following manner:—The fibre is boiled in a solution of arsenic acid and soap in the proportions of 1 per cent. of arsenic acid and 3 per cent. of soap.

“Having described the nature of my invention and the manner of performing the same, I declare that what I claim as my invention to be protected by the hereinbefore in part recited Letters Patent is, the improved process, as herein described, of treating vegetable fibre (such as cotton, flax, jute, hemp, and China grass) whereby they acquire the character and appearance of silk.”

A.D. 1876, December 1st.—No. 4655.

BUTLER, JOHN SWINTON. "Improvements in the Preparation of Aniline Dyes. (*Void by reason of the Patentee having neglected to file a Specification in pursuance of the conditions of the Letters Patent.*")

"This invention consists in an improved process for obtaining dyes from aniline compound, and is as follows, *videlicet*:—

"For preparing red, magenta, cardinal fuschine, and analogous colours, the aniline compound is dissolved in boiling water, or in its ordinary solvent, to which has been added 3 per cent. of muriatic acid with 1 per cent. of chlorate of potass. When the solution is free from the smell of chlorine gas it may be used for the tinge or shade required by taking it in the required quantity.

"For blue, Nicholson blue, violet, mauve, black and analogous colours, the above process is employed, but I use only one-half the above stated quantity of chlorohydric acid and chlorate of potass.

"The intermediate shades are obtained by mixing the different aniline salts treated as hereinbefore described in such quantity and mixture as is necessary for obtaining them."

A.D. 1877, December 5th.—No. 4696.

RYDILL, GEORGE. "Improvements in Dyeing Dark Shades of Piece Goods, Woollen Waste, Hair, and Rags a Light Fast Yellow or Fawn Colour, Dyeing Fast Aniline Blue and other Colours, Utilizing the Waste Products for Treating Sewage and Manure."

"My invention consists in the employment of nitrate of soda or nitrate of potash treated with dilute sulphuric, muriatic, or hydrochloric acid, for dyeing a fast light yellow or fawn colour, and for producing light yellow shades from once dark dyed piece goods composed wholly or in part of previously dyed wool, woollen material and woollen waste, and for dyeing piece goods, wool, woollen rags, alpaca, mohair, camels' hair, woollen flock, hair, silk rags, waste silk, rabbit or hare down, shoddy or mungo, a light yellow or

fawn colour ; also for dyeing the same when required a fast scarlet, blue, maroon, and other colours.

“ Or nitric acid and nitrate of soda or nitrate of potash are treated with dilute sulphuric, muriatic, or hydrochloric acid, for producing a fast light yellow or fawn colour ; but as nitric acid is a manufactured article by distillation, and very costly, evaporates quickly, and stains the skin, I prefer to use nitrate of soda and sulphuric acid, as they do not evaporate so quickly, neither do they stain the skin, besides being cheaper, more effectual, and not liable to turn so red with heat or alkali in cleansing, milling, and removing the acid.

“ With respect to nitrate of potash and its use in dyeing a yellow or fawn colour with acids, nitrate of soda is not only cheaper than nitrate of potash, but it has the advantage of containing 9 per cent. more of nitric acid.

“ These improvements are not only for dyeing piece goods, woollen material, hair, shoddy, mungo, and woollen rags a fast light yellow or fawn colour, but I introduce and use nitrate of soda, without any previous treatment or distillation, with acid as an useful assistant material for dyeing wool, piece goods, woollen rags, and fibrous substances fast colours by being united with dye-colouring matter.

“ I first thoroughly cleanse wool, piece goods, woollen material, alpacca, mohair, camels' hair, woollen rags, hair, silk rags, waste silk, flock, rabbit or hare down or wool, and then dye, stain, or change the colour of the animal fibres a fast light yellow or fawn colour in a cold liquid as follows :— I prepare in a vessel containing any required quantity of dilute sulphuric acid at a strength from 6° to 30° or more on Twaddell's hydrometer ; I then dissolve with water nitrate of soda, of weight according to quantity of liquid required, then mix the dissolved nitrate of soda with the dilute sulphuric acid in the vessel, place in the piece goods, wool, silk, animal hair, or woollen rags, and let them lay in the liquid a few days or a week. The time required to dye or stain the fabrics or materials a fast light yellow or fawn colour is according to the strength of the liquid, such being effected without labour or attention, except an occasional turn over with a stick. I

find by experiment that this method is one to preserve the elasticity of the fibres.

"Or I prepare in a vessel any required quantity of dilute sulphuric acid, at a strength from 6° to 30° or more on Twaddell's hydrometer, then dissolve with water nitrate of potash, weight according to the liquid required to be used, mix the dissolved nitrate of potash with the dilute sulphuric acid, place in the wool, piece goods, woollen material, alpacca, mohair, camels' hair, woollen rags, hair, silk rags, waste silk, flock, rabbit or hare down or wool, and let them lay in the liquid the required time to stain or dye the fabrics a fast light yellow or fawn colour. The time required to dye or stain with cold liquids the fabrics or fibres a fast yellow or fawn colour is according to the strength of the liquid.

"Or dilute muriatic or hydrochloric acid may be used with nitrate of soda or nitrate of potash for staining or dyeing wool, piece goods, woollen rags, animal fibres or substances a fast light yellow or fawn colour.

"Or sulphuric, muriatic, or hydrochloric acid may be used and mixed together in any required proportion with nitrate of soda or nitrate of potash or a nitrate in solution, for staining or dyeing wool, piece goods, woollen rags, animal fibres or substances a fast light yellow or fawn colour in a cold liquid, at a strength according to the time required for staining or dyeing the fibres or fabrics.

"Or I use separately or mixed together in a vessel dilute sulphuric, muriatic, or hydrochloric acid, together with any required proportions of dilute nitrate of soda or nitrate of potash liquid with dilute nitric acid, making the liquids at a strength on Twaddell's hydrometer of from 6° to 30° or more, place in the wool, piece goods, silk, woollen rags, animal fibres or substances, and let them lay in the acid liquid the time required to stain or dye the fabrics a fast light yellow or fawn colour. A small quantity of logwood, alum, salt, ammonia, potash, or caustic soda may be introduced when required to bring up the colour.

"In dyeing or staining large quantities of material with cold liquid a number of vessels, as described, require to be

charged. When the material is dyed or stained a fast yellow or fawn colour as required, it is then removed from the vessel, and the same liquid is re-used for dyeing or staining other chargings of material.

“Having described what sulphuric, muriatic, or hydrochloric or nitric acid or nitrate of soda and nitrate of potash, or a nitrate in solution will do cold, in dyeing or staining animal fibres and substances a light yellow or fawn colour, I will now explain what results such acid nitrate liquids are capable of accomplishing when made hot.

“In a vessel made of stone, wood, earthenware, glass, lead, iron, platinum, gold, or any other suitable material, I prepare any required quantity of dilute sulphuric acid, at a strength from 6° to 20° or more on Twaddell's hydrometer, then dissolve with water nitrate of soda, weight according to the quantity of liquid and strength required to be used, and then mix the dissolved nitrate of soda with the dilute sulphuric acid, or the nitrate of soda may be dissolved in the prepared acid liquid, which acid liquid I heat with steam passing through a coil of lead pipe or a jacketed vessel, or a vessel heated with water or steam acting on the outside; heat from mineral or vegetable oils, fire, gas, waste products of combustion; or a vessel may rest on a hot hearth, or hot air may be used, either to pass through the acid liquor or to act on the outside of the vessel, to heat the same. When the acid liquid in the vessel is made hot I place in the wool, piece goods, silk, animal fibres, hair, yarns, or woollen rags, which may have been previously dyed blue, green, scarlet, black, or any other colour, when the same becomes dyed or stained a light yellow or fawn colour in the short space of from one minute to five, ten or more minutes, according to the strength and warmth of the material to be dyed.

“If a quantity of material is introduced wet and cold it is not stained or dyed so quickly as when the material is warm or taken from hot water and the surplus moisture removed with a hydro-extractor; but under all circumstances piece goods and materials to be dyed, stained, or the colour changed are entirely under the control of the person in attendance.

"Or I prepare a liquid of any required strength with muriatic or hydrochloric acid and nitrate of soda to dye or stain wool, piece goods, animal fibres, hair, yarns, or woollen rags a fast light yellow or fawn colour by heating the acid liquid, as herein described.

"Or sulphuric, muriatic, or hydrochloric acid may be mixed together in any required proportions with nitrate of soda for dyeing or staining wool, piece goods, silk, animal fibres, hair, yarns, rabbit or hare down or wool, or woollen rags a fast light yellow or fawn colour with hot acid liquid, as herein described.

"Or dilute sulphuric, muriatic, or hydrochloric acid may be used each separately with nitrate of potash in any required proportion for dyeing or staining wool, piece goods, animal fibres, and woollen rags a fast light yellow or fawn colour.

"Or dilute sulphuric, muriatic, or hydrochloric acid are mixed together in any required proportions with nitrate of potash for dyeing or staining wool, piece goods, animal fibres, and woollen rags a fast light yellow or fawn colour with hot acid liquid, as herein described.

"Or dilute sulphuric, muriatic, or hydrochloric acid may be mixed with either nitrate of soda or nitrate of potash and dilute nitric acid at any required strength or in any required proportions of one to each other, and heat the same as herein described, for dyeing or staining wool, piece goods, silk, animal fibres, hair, yarns, or woollen rags a fast light yellow or fawn colour. A small quantity of logwood, alum, salt, ammonia, potash, or caustic soda may be introduced when required to bring up the colour, or other colouring liquids or substances may be mixed with the nitrate liquids; also borax is advantageously used.

"When piece goods and animal fibres to be dyed or stained a fast light yellow or fawn colour are perfectly free from dye colouring matter, such as white piece goods, wool, or white woollen rags, I then mix with dilute sulphuric, muriatic, or hydrochloric acid nitrate of soda or nitrate of potash, a little logwood, or any other dye-colouring matter or spent dye

liquors, may be utilized for the acids to act upon, or dye refuse, bark, or other colouring substances may be employed to feed the acid or acids, nitrate of soda or nitrate of potash, or a nitrate in solution with colouring matter or sulphuric, muriatic, or hydrochloric acid liquids which have been used for saturating shallies, linsey skirting or woollen rags, previous to and for removing vegetable substances from woollen material by means of heat (called extracting), and which acid liquids contain a little dye-colouring matter removed from the rags while being steeped or saturated in acid liquid.

“By experiments I find these acid liquids to be most useful, and cause the acid or acids to serve for two purposes; or aniline or other colours may be introduced to colour and dye with.

“In dyeing aniline and other colours fast on piece goods, wool, and other animal fibres and substances, I use nitrate of soda or nitrate of potash, which I find most useful agents, particularly the nitrate of soda for its cheapness and effect. For example, I place in a vessel of hot water aniline blue and nitrate of soda; I then put in the wool, piece goods, woollen rags, extract wool or other animal fibres or substances to be dyed, and boil for five, ten, or thirty minutes; I then raise the material and pour in a small quantity of dilute sulphuric acid, which with the nitrate of soda causes the aniline blue colour to become fast on the fabrics, so that the aniline blue will stand the test of nitric acid, muriatic, or hydrochloric or sulphuric acid without the colour being effected. Maroon and other colours are dyed fast with a like result; also dark dyed coloured piece goods, shoddy, mungo, and woollen rags are readily dyed fast blue.

“By steeping or saturating piece goods, wool, silk, animal fibres, woollen or linsey rags, composed partly of animal and vegetable fibres and substances, in dilute sulphuric, muriatic, or hydrochloric acid, and nitrate of soda, liquid or dilute sulphuric, muriatic, or hydrochloric acid, and nitrate of potash liquid mixed together in any required proportions, after removing surplus liquid and steaming the fabrics or material in a steam-tight room or drying the same with heat or steam

of 120° or more, the cotton or vegetable substances are destroyed, and the fabrics or material are changed, stained, or dyed a light yellow or fawn colour. When the piece goods or fabrics are to be steamed I make the liquid into a kind of liquid paste with starch.

“By this improvement dark dyed mixed coloured woollen materials and hair which would serve only for some common purpose if made into piece goods and yarns, are dyed into a light yellow or fawn colour, which colour can now only be obtained from white wool, alpacca, mohair, or light valuable shades of woollen materials or hair.

“Another advantage is that mixed woollen waste containing almost every colour, woollen piece goods as well as woollen rags, are dyed or stained a light yellow or fawn colour, which when pulled up by a rag or Garnett machine, and then carded, one even colour is produced. Not only this, but a light foundation or ground is formed for redyeing any other light colours or light shades upon the fabrics or materials, so that cloth, blankets, carpets, and other woven or knitted fabrics are thereby produced at a most reasonable cost and the process of dyeing simplified.

“The following classes are some of the materials which contain mixed, dark, and faded colours, much enhanced in value when dyed a light yellow or fawn colour, such as:—Scotch and other woollen waste, hosiery waste and clippings, alpacca, mohair, shirtings, French merinoes, coloured flannels, coloured serges, woollen fringe, woollen braids, coburges, woollen comforters, extracted linsey stockings, indigo stockings, extract wool, hard stuffs or woollen skirting, coloured stockings, cloth rags, extracted waste silk, silk rags, flocks, rags, and other woollen materials.

“It has been shown by many careful and accurate experiments that nitrogen in the form of nitric acid exerts a more powerful influence on the growth of graminea than an equal weight of nitrogen in the form of ammonia, and that the application of nitrate acts on grains and grasses in the growing seasons with extraordinary rapidity, and its action is not so much diminished by rain. I therefore cleanse the dyed or

stained fabrics or materials when nitrate of soda is used from the nitrate or nitric acid with cold or hot water, ammonia, potash, lime water, borax, caustic soda, or other alkali, and utilize the same for treating sewage, liquid manure for growing crops, or watering manure, earths, ashes, refuse, animal charcoal, or other manural substances to retain the nitrate or nitric acid, or nitrate of ammonia.

“The dirty or spent acid liquids or condensed vapours, in dyeing or staining yellow, I also utilize for treating sewage, growing crops, or manure as described, so that the nitrate of soda, nitrate of potash, and acids, ammonia, and other alkalies, which in the first instance are rather expensive, are not wasted, but turned to useful purposes instead of a nuisance.

To bring up the spent liquids and make them useful after once used in dyeing or staining fabrics or materials a fast light yellow or fawn colour with dilute sulphuric, muriatic, or hydrochloric acid and nitrate of soda liquid, or dilute sulphuric, muriatic, or hydrochloric acid and nitrate of potash, or dilute sulphuric, muriatic, or hydrochloric acid mixed with nitrate of soda or nitrate of potash and dilute nitric acid, I place in the vessel or vessels containing the acid liquid or liquids iron borings, filings, or turnings, refuse card wire, or scrap iron, which convert the acid liquids into nitrate of iron or nitro-sulphate of iron, or other valuable chemical products are formed with the acids, alum, salt, and alkalies. Sulphate of iron and nitrate of iron produced from those refuse acid chemicals are most useful in dyeing.

“And having now described the nature of my said invention, and in what manner the same is to be performed, I declare that I claim as my invention,—

“Firstly. The dyeing, staining, or changing the colour of wool, woollen waste, hair, silk, woollen rags, animal fibres, and materials, in a vessel, a light fast yellow or fawn colour, either in a cold or hot dilute sulphuric, muriatic, or hydrochloric acid and nitrate of soda liquid, and removing such dye or colouring surplus liquid with water and alkalies, as herein described.

"Secondly. The dyeing, staining, or changing the colour of woollen piece goods, animal fibres, and substances, in a vessel with dilute sulphuric, muriatic, or hydrochloric acid and nitrate of potash, a fast light yellow or fawn colour, as herein described.

"Thirdly. The dyeing, staining, or changing the colour of woollen piece goods, animal fibres, and substances, in a vessel with dilute sulphuric, muriatic, or hydrochloric acid and dissolved nitrate of soda, nitrate of potash, and nitric acid, being mixed one with the other and forming a cold or hot acid liquid, for dyeing, staining, or producing in various ways a fast light yellow or fawn colour, as herein described.

"Fourthly. The use of nitrate of soda or nitrate in solution in dyeing or staining animal fibres and materials fast colours, with aniline or other dye colouring matter, and steaming the animal fibres and materials in a room, as described.

"Fifthly. Heating the water or dye liquid with hot air passing through the liquid or through a coil of pipe or a jacketed vessel, or heating the same as herein described.

"Sixthly. Utilizing the sulphuric or muriatic or hydrochloric acid liquid used in saturating animal fibres and substances for extracting, as well as the use of alum, salt, ammonia, potash, caustic soda, and spent dye liquids, as herein described.

"Seventhly. Producing dye colouring matter with the refuse acid nitrate chemical acting on metal, as herein described.

"Eighthly. The utilizing of the refuse acid nitrates and alkalies as a manure, or for treating sewage water, as herein described.

In witness whereof, I, the said George Rydill, have hereto set my hand and seal, this first day of June, in the year of our Lord, one thousand eight hundred and seventy-seven."

A.D. 1876, December 7th.—No. 4729.

FULTON, DAVID. "Improvements in Machinery for Engraving Printing Rollers." (*This Invention received Provisional Protection only.*)

"This invention relates to machinery for engraving printing rollers by means of small steel milling rollers, and has principally for its object to secure rapidity and accuracy of operation by automatic means in cases in which the action of the milling roller is interrupted, in order that the device which it indents or engraves may be applied to separate spaces.

"Heretofore, in attempts to attain the results now aimed at, the printing roller has been made to rotate continuously at a uniform rate, the milling roller being raised from and lowered down upon the printing roller by means of an eccentric or cam, but such mode has failed to give sufficient accuracy, and the desired results have had to be approximated to by very careful, skilful, and tedious manipulation of the machinery.

"By the present invention the printing roller is driven intermittently, and is brought completely to rest between each action of the milling roller. The space on the printing roller on which the milling roller acts at each operation is determined by a cam or eccentric which lifts the milling roller, and the interval unacted on, if any, is determined by the extra extent of the movement of the printing roller beyond the point at which the milling roller is lifted. The printing roller is then stationary for a sufficient time, during which the milling roller redescends upon it and must come in contact with it in the precise position required, so that on the printing roller moving forward again the milling action starts accurately as desired.

"After each action, and whilst the printing roller is completing its extra movement corresponding to the part to be unacted on, the milling roller is turned back to its proper position for starting by a weighted lever attached to it, and provided with a striking point to encounter a stop, the striking point being adjustable by a screw so that the proper position of the milling roller may be accurately secured.

"The printing roller is carried in a usual manner in the machine, and is turned by a train of toothed wheels which can be changed to suit different sizes of rollers and other circumstances.

"The intermittent motion is obtained, according to one modification, by means of a pair of wheels, the driving one of which has a part of its rim toothed, and a part plain or untoothed, the latter part corresponding to the period during which the printing roller is stationary. The driving wheel is formed with one or more series of teeth to gear with the teeth of the driver, and with a very short blank space between the end of one series and the beginning of the next; and the sets of teeth are brought to gear successively with each other by single larger teeth fixed in suitable positions at the sides of the rims having the small teeth. Instead of the wheels just described, what are known as Swiss wheels or any other known arrangement for giving a suitable intermittent motion may be adopted.

"The milling roller may be carried as in any suitable arrangement of existing machinery for continuous milling work, but it is by preference held by a lever centred on a bracket or standard formed on or attached to the longitudinally sliding carriage, such lever having on the back or further side of its fulcrum an arm connected by a link to a weighted lever below, an arrangement more convenient and less in the way of the attendant worker than that ordinarily adopted. The cam or eccentric by which the milling roller is lifted off the printing roller is by preference arranged to act on the lower weighted lever.

"It is an important advantage of the hereinbefore described improvements that the operation known as 'rocking,' by which the indenting action of the milling roller is repeated, can be performed without in the slightest degree interfering with the accuracy or rapidity with which the work may be continued between the rocking operations."

A.D. 1876, December 7th.—No. 4741.

WISE, WILLIAM LLOYD. "Improvements in Machinery for Drying Yarn." *A communication from C. H. Weisbach.*

"This invention refers to machinery by which all sorts of yarns may be dried.

“Heretofore hot air has been mostly made use of for drying yarn, it being customary to hang the hanks in drying rooms and to admit air at a high temperature into them to accomplish the purpose. This mode of drying is subject to many inconveniences. In the first place, drying rooms are liable to conflagrations; the goods contained in such rooms frequently become ignited and are consumed by fire notwithstanding that every care is taken to avoid such calamities. The hot air drying process is frequently most injurious to the quality of yarns in more than one respect. Dyed yarns suffer in the finer tints of color more particularly when yarns of different colors are dried together in one room, where the colors are frequently subject to what is known to dyers as breaking out, and yarns of light colors are liable to become spotted. Hence a general desire has become manifest for drying yarns in a convenient, expeditious, and cheap manner, which will at the same time obviate the injurious effects of drying by hot air. This general want is in every respect met by the present invention.

“In the machinery employed the principle is adopted of rotating yarn in the air during a certain time, thus accomplishing the drying in a satisfactory manner, the machine being constructed in such manner that the hanging up and taking off of the hanks can be effected in the most convenient and expeditious way, and so that hanks of different lengths may be hung in the machine for drying. These drying machines may be worked in moderately warm rooms, which will assist the drying process, but the use of hot air is absolutely excluded as being injurious and dangerous.

“In one arrangement of machine two frames or standards carry bearings at their upper part in which works a shaft. On this shaft, near each end, a nave constructed with arms is keyed. Each nave is supplied with four or more arms, which may be radial or slanting.

“The arms are constructed with bosses at their outer ends through which centre pins are passed, the inner ends of which centre pins are pointed. These centre pins are held in place by nuts. The bosses of the arms at one end of the machine

are threaded for the reception of their centre pins. These last mentioned centre pins are made with square heads on their outer ends to receive a key for turning them in their bosses, and they are secured therein by the nuts on the outer sides of the bosses.

"Every two pointed centre pins in the ends of arms opposite each other carry between them a roller, preferably of wood, of octagon or suitable shape, and which rollers have central holes or recesses to receive the pointed ends of the centre pins.

"The arms of the naves are formed with slots which extend along the greater parts of the lengths of the arms; into these slots are fitted sliding blocks or cheeks having screw bolts passing through them, by means of which each block or cheek can be secured at any point of the slot in its arm. Each block or cheek is constructed with a boss similar to the one at the end of the arm; at one end of the machine each block or cheek carries a firmly screwed centre pin and at the other end of the machine each block or cheek carries an adjustable centre pin as described with reference to the ends of the arms. These centre pins carry rollers between them as described with regard to the other centre pins. Thus the hanks of yarn can easily be hung over two rollers as described, which are then placed between the corresponding pointed centre pins and secured in their position by means of the adjustable screws. It likewise follows that the distance of the rollers from each other may be regulated to suit the length of the hanks and the degree of stretch that is to be given to the yarn. The hanks having thus been introduced into the machine the same can be set in motion by passing a strap on to a fast pulley of the main shaft and driving the same as may be desired.

"A loose pulley and disengager are provided for stopping the machine. The radial position of the hanks to the rotary motion affords advantageous results as regards the speed of the drying process, and the system of drying yarns generally by thus merely swinging them in the air has no injurious influence of any kind with regard to the color and cleanness.

“I now proceed to describe a modification of this invention in which a ventilator or blower is introduced inside of the drying machine, the object being to blow the air outwardly through the hanks of yarn on the rollers and thus materially to assist the process of drying.

“Suitable frames carry bearings for the naves of two sets of large arms; the horizontal shaft resting in these naves is rotated by pullies and carries the ventilator or blower, the wings of which nearly equal in length the length of the shaft.

“The two sets of large arms are connected together by connecting stays, so that they form as it were one body. A sleeve of the one set of arms is of considerable length, projects beyond the corresponding frame, and there carries pullies for giving a slow rotary motion to the reel round about the ventilator or blower shaft, but in opposite direction to the motion of the latter. The six or eight arms of each set are placed radially to the centre, but outer arms or extensions are placed in slanting or angular positions to the radial arms. The radial arms at one end of the machine carry small shafts or spindles made to turn parallel with the main shaft, and which carry at their outer ends little star wheels. The inner ends of these spindles are made each with a projecting square or prismatical head so that rollers can be easily fixed on them, which rollers extend to the arms at the other end of the machine, to which they can be readily attached by means of adjustable centre pins.

“When the entire reel is rotated the rollers rotate as well, and the little star wheels striking against a bolt or projection fixed to the frame are advanced intermittently by one or more teeth, hence the rollers are by degrees rotated. The hanks of yarn to be dried being hung in the arms, and the latter in position, they are circulated by the slow motion given to the reel, and are dried by the current of air proceeding from the ventilator or blower, and as the rollers themselves are slowly moved on the hanks, are made to continually change their position, and hence no unequal drying takes place.

“In order to prevent entanglement of light yarns in hanks,

which might be occasioned by the sharp current of air and in consequence of too great proximity, the outer or slanting parts of the arms may be made use of. They are made with slots in which cheeks or blocks are made to slide, containing centre pins such as herein-before described, between which rollers can be inserted, on to which one end of the hanks of yarns can be hung, so that, for example, each hank can be hung on the inner roller of the first arm and on the outer roller of the next or second arm, thus entanglement will be effectually prevented."

The above is the provisional specification, from which a general idea of the improvements can be obtained, the complete specification refers to drawings which accompany it.

A.D. 1876, December 8th.—No. 4756.

WILSON, ROBERT. "An Improved Mode of Finishing Cotton Fabrics."

"My invention consists in imparting the required finish to cotton fabrics by cylinders or rollers revolving alternately in contrary directions, whereby the required finish is obtained more expeditiously and economically than by the machinery now in use.

"In performing my invention I take the cotton fabrics, either bleached or unbleached, and either with or without starch, size, or stiffening, and wind them on a roller or beam. The roller or beam, with the fabric so wound on, is placed between two cylinders or rollers with the line of their axis parallel to each other to compress the fabric; these cylinders or rollers are made to revolve alternately in opposite directions, as described in the Specification of former Letters Patent granted to me on the 17th day of May, 1871, No. 1335; the cloth or fabric being compressed between the two cylinders or rollers is also moved with or by them alternately in contrary directions with its beam or roller, and this alternate motion combined with the pressure produces friction in the cloth or fabric, and consequently heat is evolved, which produces the finish required.

"I wish to remark that this alternate motion may be ob-

tained by placing the cloth on the roller or beam between two flat surfaces, both of which traverse two and fro, or only one of which traverses to and fro, as in an ordinary mangle; but as this mode of operation is so slow, and uncertain as to results, I prefer the mode first described."

The above is the provisional specification, the complete specification is illustrated by a drawing.

A.D. 1876, December 14th.—No. 4839.

GIRARD, CHARLES and others. "Improved Processes for Obtaining Colouring Matters, or of Processes for obtaining Novel Colouring Matters."

"When preparing certain colouring matters in accordance with our invention we heat together any of the phenols or diphenols, and any or certain of the diatomic acids, such for example as oxalic, tartaric, citric, lactic, succinic, camphoric, or phtalic acids, either with or without the addition of sulphuric acid, until a reaction takes place. We then treat the product with a solution of hypochlorite, hypobromite, or hypiodite of an alkali, or of an alkaline earth, or of products capable of producing the oxygenated derivatives of chlorine, iodine, or bromine, such for example as mixtures of alkaline, chlorate, iodate, or bromate, with chlorhydric, bromhydric, iodhydric, or fluorhydric acid, or their salts, or of nitric and chlorhydric, or nitric and bromhydric acids, or of nitric and iodhydric or nitric and fluorhydric acids; for example, when we heat at a temperature of about two hundred degrees centigrade a mixture of twenty-two parts of resorcine, and fifteen parts anhydrous phtalic acid, we obtain phtalic fluorescine which we dissolve in an alkaline solution. To this solution we add by degrees a solution of hypochlorite containing more or less of free chlorine, according to the shade of colour required. We then saturate the solution with an acid, and carbonic acid is set free. When the mixture is filtered and the precipitate is washed a colouring matter is obtained which we style yellow aureosine. Alkaline solutions of this matter appear yellow green by reflected light, and a rose colour by transmitted light. When we use a hypobromite or

hypoiodite, or a mixture of the salts in place of the hypochlorite, we obtain a colouring matter which we style red aureosine. From these products we obtain other colouring matters by treatment with nitric acid diluted with about twice its volume of water, the mixture being heated. When the required shade is attained the colouring matter is precipitated by means of chloride of sodium, and the resulting precipitate is recovered by filtration. The product of this treatment, which we style yellow or red rubeosines, according as they are prepared from the yellow or red aureosines, are soluble in alkaline solutions, which they render a deep crimson colour.

"We also obtain colouring matters of various shades by causing a reaction between the hypochlorites, hypobromites, or hypoiodites of alkalies or alkaline earths, and the methylic, ethylic, amylic, benzylic, or acetylic derivatives of resorcine, combined with a diatomic acid, as for example, with anhydrous phtalic acid, or we obtain analogous matters by causing a reaction between the iodide, bromide, or chloride of an alcoholic radical, such as methyl, ethyl, amyl, or benzyl, and the aforesaid yellow or red aureosine or rubeosine.

"By treating with nitric acid or chromic acid, eosine or primrose, or other of the bromated derivatives of phtaleine, resorcine, or other diphenol, or their methylated, ethylated, or acetylated derivatives, under the same conditions as when treating the aureosines in the manner hereinbefore indicated, we obtain colouring matters analogous to those obtained by the treatment of the red aureosines. Also when treating eosine or the bromated derivatives of phtaleine with a mixture of acetate of soda and acetic acid under pressure, at a temperature of about two hundred to two hundred and twenty degrees centigrade, we obtain products analogous to the red aureosines.

"By the methods and means herein indicated we obtain colouring matters varying in shades from yellow through orange to intense red.

"Having now set forth and indicated the nature of our said invention, and the manner in which we carry the same into

practical effect, we would in conclusion have it to be understood that we claim,—

“First. The methods of producing colouring matters, substantially as set forth and indicated.

“Secondly. The method of producing the colouring matter which we style yellow aureosine, substantially as set forth and indicated.

“Thirdly. The method of producing the colouring matter which we style red aureosine, substantially as set forth and indicated.

“Fourthly. The method of producing the colouring matter which we style yellow rubeosine, substantially as set forth and indicated.

“And, lastly. The method of producing the colouring matter which we style red rubeosine, substantially as set forth and indicated.”

10. British and Foreign Patents, from the Commissioners of Patents Journal, June 26th to July 20th 1877, inclusive.

Manufacture of Colouring Matters.

2602. WILLIAM ROBERT LAKE, of the firm of Haseltine, Lake, and Co., Patent Agents, Southampton Buildings, London, for an invention of “An improved manufacture of red colour.”—A communication to him from abroad by Johann Zeltner, of Nuremberg, Bavaria.—Dated 5th July, 1877.
2614. WILLIAM ROBERT LAKE, of the firm of Haseltine, Lake, and Co., Patent Agents, Southampton Buildings, London, for an invention of “Improvements in the manufacture of violet colour.”—A communication to him from abroad by Johann Zeltner, of Nuremberg, Bavaria.—Dated 6th July, 1877.
2649. ADALBERT WACHHAUSEN, of Wiesbaden, Germany, Doctor of Philosophy, for an invention of “An improved brown colour or dye and process for obtaining the same.”—Dated 10th July, 1877.

2347. EDOUARD GEORGE PETER THOMAS, of the Star Chemical Works, Brentford, in the county of Middlesex, for an invention of "Improvements in the manufacture of blue colouring matter."—A communication to him from abroad by Charles Adam Girard, of 20, Rue des Ecoles, Paris, in the Republic of France.—Dated 4th July, 1874.—This patent has become void.

186,032. H. CARO, of Mannheim, Germany, for obtaining colouring matter suitable for dyeing and printing."—Application filed 2nd October, 1876.—United States patent.

Processes of Printing and Dyeing.

84. WILLIAM BIRCH, of Salford, in the county of Lancaster, Machinist, for an invention of "Improved self-acting machinery for opening, smoothing, spreading, and guiding fabrics for the use of bleachers, dyers, calico printers, and others."—Dated 8th January, 1877.—This patent has passed the great seal.

266. JAMES CHADWICK, of the Spring Brook Print Works, Chadderton, in the county of Lancaster, for an invention of "Improvements in printing textile fabrics."—A communication to him from abroad by James Harley, of Lowell, Massachusetts, United States of America.—Dated 20th January, 1877.—This patent has passed the great seal.

2513. WILLIAM MORGAN-BROWN, of the firm of Brandon and Morgan-Brown, Engineers and Patent Agents, of 38, Southampton Buildings, London, and 1, Rue Lafitte, Paris, for an invention of "Improvements in printing textile fabrics."—A communication to him from abroad by Henry Dow Dupree, of Boston, county of Suffolk, state of Massachusetts, United States of America.—Dated 29th June, 1877.—Provisional protection has been granted.

2399. THOMAS PATERSON MILLER, of the Cambuslang Dyeworks, in the county of Lanark, North Britain, has given notice to proceed in respect of the invention of "Improvements in or connected with the process of dyeing yarn or cloth with alizarine or analogous colouring matters."

2389. ALEXANDER MELVILLE CLARK, of 53, Chancery Lane, in the county of Middlesex, Patent Agent, for an invention of "Improvements in printing fabrics."—A communication to him from abroad by Antoine Bozzini, of Lyons, France.—Dated 7th July, 1874. This patent has become void.

- 42,371. G. RYDILL, for "Improvements in dyeing pieces of stuff, woollen waste, &c."—Dated 4th June, 1877.—Belgian patent.

Yarn Treatments.

698. JOHN STIRLING ALSTON, Merchant, and WILLIAM REID, Dye Works Manager, both of Glasgow, in the county of Lanark, North Britain, have given notice to proceed in respect of the invention of "Improvements in apparatus to be used in connection with various processes of treating yarns with liquids."
964. ARCHIBALD STEWART BYERS, of the firm of "Campbell and Byers," of Paisley, in the county of Renfrew, North Britain, Dyers, has given notice to proceed in respect of the invention of "Improvements in scouring, bleaching, and dyeing yarns, and in the machinery or apparatus employed therefor."
2311. JOSEPH MANCHESTER, of Manchester, in the county of Lancaster, and WILLIAM ALFRED TURNER, of Pendleton, in the same county, Cotton Manufacturers for an invention of "Improvements in apparatus for gassing yarns and fabrics."—Dated 2nd July, 1874.—This patent has become void.
1840. THOMAS PATERSON MILLER and DAVID MILLER, both of Cambuslang Dyeworks, in the county of Lanark, North Britain, for an invention of "Improvements in apparatus for dyeing or otherwise treating yarns."—Dated 28th June, 1870.—This patent has become void.
- 185,625. WM. CLARK, of Newark, N.J., for "Processes and apparatus for dyeing thread and yarn."—Application filed 18th November, 1875.—United States patent.

Claim.—1. The improvement in the art of dyeing thread in the skein, consisting in the connecting of the skeins in a chain by threads or interposed links so slender as to enable the skeins to take the dye equally throughout, the dipping of said chain of skeins progressively into the dye-liquor, and expression of the superfluous liquor therefrom, all substantially as before set forth. 2. The combination, substantially as before set forth, of the dye-vat, the guide, the dipping-roller, the squeezing-roller, and the belts by which the dipping-roller and the squeezing-roller are caused to revolve positively. 3. The combination, substantially as before set forth, of the dye-vat, the dipping-roller, the squeezing-rollers, the delivery-roller, and the belts by means of which the several rollers are caused to revolve positively. 4. The combination, substantially as before set forth, of the dye-vat, the guide, the dipping-roller, the squeezing rollers, the delivery roller, and the belts by means of which the several rollers are caused to revolve positively.'

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*1. Notes upon Aniline Black.**

BY M. G. WITZ.

Upon the Chemical Properties of Aniline Black resulting from Oxidation by means of Chlorates.—The observations which I have noted in this part of my paper are far from constituting a complete and systematic account of the important colour which still occupies so much attention, although the literature upon the subject is already so extensive. They consist of a simple series of experiments carried out at different times upon aniline blacks printed upon calicoes with pure materials at known degrees of strength. I shall afterwards return to shew the method which has been followed in obtaining them, because, in my opinion, it allows the study of the special influence of reagents to be carried on with more exactness and certainty than has hitherto been the case.

The blacks and greys from phenylamine, that is, derived from pure aniline by oxidation through the medium of chlorates, having been simply washed off, then soaped, and greened by pure hydrochloric acid, preserve their grey blue shade when they are kept in pure boiling water.† This is the

*Bull. de la Soc. Ind. de Rouen, v., p. 238. Continued from Textile Colourist, iv., p. 1.

†The colour equals the blue-violet with $\frac{1}{10}$ black of Chevreul's nomenclature in the wet state becoming when dry 5 blue with $\frac{1}{10}$ black when the muriate of aniline is in excess, and 1 blue with $\frac{1}{10}$ black when the chlorate is in excess.

true colour of the substance frequently called emeraldine, which we shall provisionally call *acid aniline black*, for it has always a more decided green shade when the acid is in excess, as at the moment of its formation.

The same samples not greened, that is, washed off only in a bath of alkali or chromate—one or other of which baths are at the present time used for this colour in practice—invariably preserve their respective shades of blue-black and violet-black when kept in pure boiling water.

We may note in passing that the contact with pure hydrochloric acid at 23° Tw. destroys immediately in the cold the violet-black produced by the supplementary oxidation of aniline black, as for example by the treatment with bichromate of potash, and brings it to a state corresponding to the ordinary blue-black. Weaker acids have the same action, but operate more slowly unless they are warmed.

Acids and Aniline Black.—The influence of various acids upon the blacks previously washed off and considered as neutral is too well known to require notice except in a general manner.

The weaker acids, such as carbonic acid, have no action.

Acids of a stronger nature, but not very powerful, such as acetic acid and many organic acids, turn the black green.

Lastly, the strong mineral acids, even when very largely diluted with water, such as hydrochloric acid, or when they are not completely saturated by a base as sulphuric acid in bisulphate of potash, all turn the common aniline black into green.

The highly oxygenated acids—chloric acid, perchloric acid, nitric acid—possess also the same property when they are not too concentrated or applied too warm. The action of some of the highly oxygenated acids with a metallic radical—chromic acid, permanganic acid—will be separately examined when treating of oxidizing agents.

There are still other acid bodies which come under the class of deoxidizing agents, and will be studied with them; such are sulphuretted hydrogen, sulphurous acid, and hydro-sulphurous acid.

The action upon aniline black of salts which have an acid reaction to litmus, and of certain salts generally considered as neutral, demand a close examination.

Action of Muriate of Aniline.—The normal solution contains 13 per cent. neutral salt. Another solution was acidified with $\frac{1}{10}$ of hydrochloric acid, and to a third solution $\frac{1}{10}$ of free aniline was added. The action was tried upon blacks and greys from phenylamine which had been washed off, soaped, and chromed in the state of violet-black.

The moist samples placed in the three aniline solutions above mentioned were immediately and strongly greened.

The chrome black gives a green a little more grey in the neutral and alkaline solution; while in the acid solution there is scarcely any difference in the greening between the chromed black and a sample of blue-black washed off without chroming.

From these experiments it is seen that aniline black becomes green with both neutral and basic salts of the alkaloid, precisely the same as litmus is reddened under the same circumstances, while aniline mauve and methylaniline purple (*violet de Paris*), behave in quite a different manner. On the one hand, these two colouring matters are not changed by the neutral salts of the alkaloids, while on the other, they change to blue and to a green more or less yellow in the presence of free acids. Lastly, the alkaloids neutralize completely the action of strong acids upon these colours, while on the contrary they are without action upon the greened aniline black.

From these simple experiments it is further evident that it is impossible to avoid the greening of ordinary aniline grey and black when these are placed in solutions where aniline black is being formed by the aid of any chlorate, and that not only because such solutions always contain a free acid, but by the fact, sufficient in itself, that the solutions contain muriate of aniline which has not fully undergone transformation.

Another evident consequence confirming conclusions long ago affirmed, but seriously disputed, is that aniline black is

not greened on account of any deoxygenizing influences, but that in reality it changes its shade under the influence of acids, and notwithstanding the oxidizing action, both acidity and oxygenizing influences being indispensable for the production of this same aniline black.

Action of Salammoniac.—The solution contained 25 per cent. of salt. This salt in a pure state possesses a certain tendency to dissociation when its aqueous solution is heated, allowing a small proportion of ammonia to escape; the litmus which may be added to the liquid in order to colour it assuming a violet-red colour, while at the same time red litmus paper becomes blue when held in the disengaged vapours. Account, therefore, must be kept of this tendency, and care taken to counteract its influence by maintaining a very slight excess of ammonia in the solutions used in the experiments, so as to keep the blue litmus in a state shewing neutrality.*

Even in the cold the blacks and greys of phenylamine in the blue-black state change in salammoniac to green-blue, but do not acquire the dark green shade which is produced by strong acids. The aniline black appears to displace a small portion of the ammonia in the salammoniac.

The same specimens washed, soaped, and chromed which are in the violet-black condition, change slightly towards a bluer shade of violet; this action is evident when the experiments are made comparatively. There is a marked greening of ordinary aniline blacks which are steeped in solution of salammoniac and exposed to sunlight.

Neutralization of Acid Aniline Black by Ammonia.—When a specimen of aniline black which has become greened spontaneously in the air is sprinkled with ammonia, the black colour is temporarily restored, but it is observed that after drying the green parts reappear, as if the alkali was powerless to counteract in a permanent manner the influence of the acids which caused the greening.

* The escape of ammonia during the boiling of aqueous solution of salammoniac has been observed by Fittig, who estimated it at $1\frac{1}{2}$ per cent. (*Ann. der Ch. und Pharm.* cxxxviii., p. 189. *Dict. de Ch. Wurtz*, i. p. 221.

To demonstrate this fact in a satisfactory manner some specimens of phenylamine blacks and greys, washed, and soaped, then turned green by a normal solution of pure hydrochloric acid were restored to the blue-black shade by contact with free ammonia or by a cold solution of sesquicarbonate of ammonia. They were washed with distilled water, and, after draining for ten minutes, the remaining water was pressed out and filtered. It showed no trace of chlorides to the nitrate of silver test, and yet the samples rapidly dried in warm air required afresh a weak green-blue colour; with a sharper heat the return of the green is more evident. Experiments upon the same samples which had not previously been greened by hydrochloric acid demonstrated that the ammonia itself had no action upon the blue-black.

The same colours changed to green-blue by solution of salammoniac are not modified by washing with cold water nor by weak soap solution at the boiling point; but when passed in boiling distilled water, with or without addition of clear lime water, they become blue-black after drying.

It seems very possible, after what has been said, that the aniline black retains strongly, notwithstanding washing in cold water, a small quantity of salammoniac. By drying, and especially by heating, this salt disengages a part of its ammonia, and thus forms an acid aniline black recognisable by its hue.

Other earthy or metallic chlorides which do not affect blue litmus may possess an analogous action upon aniline black, owing to partial dissociation of their elements.

Oxidizing Agents and Aniline Black.—We may briefly recall to mind that, in principle, acid oxidizing agents alone (or neutral in presence of a trace of acid to commence with) are able to transform aniline salts into aniline black, and that very easily when the solutions are sufficiently concentrated.* We may add that oxidizing agents, whether acid, neutral, or alkaline, provided they are sufficiently energetic, may any of

* If the aniline salts are very acid, the black is not so easily formed; if they are alkaline, dark coloured bodies are produced, but not aniline black.

them act upon aniline black in many essentially different ways :—

(1) They modify the nature of the ordinary blue-black, transforming it into violet-black. These two conditions of the black are, as we have said, permanent even at the temperature of boiling water.

All supplementary oxidation to which the black may be subjected, in contact with different oxidizing agents, may be explained as simply a new state of dehydrogenation of this substance, and this should be noted once for all. When hydrochloric acid, at 23° Tw., is employed to restore the black to its original state, after its second oxidation, it is probable that there occurs a partial destruction of it by the formation of a soluble chlorinated body.

(2) When the action of the same oxidizing agents is prolonged the aniline black is gradually destroyed, passing through some intermediary stages which we shall notice ; this progressive destruction is much slower with aniline black than with indigo ; it takes place indifferently upon the neutral violet-black, or upon the corresponding acid black, according as the oxidizing baths are neutral, alkaline, or acid.

Lastly, it is observed in the majority of cases (as in heating with chromic acid, or with chloric acid and peroxide of manganese ; as in experiments upon aniline grey, insensible to the action of acids, or with chlorate of copper in the same conditions, or even with strong and cold chloric acid), that there is a partial transformation of the aniline black into a mixed product (as of the residue of oxidation) of a somewhat pale buff colour, or of an ash or yellowish grey, which has extraordinary powers of resistance to various agents.

The principal oxidising or dehydrogenizing agents may be somewhat arbitrarily classed in the six following groups ; we shall afterwards examine, more in detail, the phenomena to which they give rise.

(a) Ozone ; chlorine ; alkaline solution of hypochlorites ; nitrites, both acid and alkaline ; peroxide of hydrogen.

(b) Oxygenated compounds of chlorine, inferior to chloric acid, as chlorous and hypochloric acid ; chloric acid, plus

hydrochloric acid ; or chlorates with acids, along with traces of vanadium, copper, cerium, or certain other metals which accelerate, in a more or less powerful manner, the decomposition of chloric acid.

(c) Permanganic acid ; neutral or alkaline permanganates ; acid vanadates.

(d) Chromic acid or acid chromates.

(e) Soluble ferricyanides.

These salts transform the blue-blacks into violet-blacks. Red prussiate of potash (ferricyanide of potassium), with addition of pure soda, carries on the oxidation of the black until it becomes red, same as with the hypochlorites, but it does not go on to the bleaching or total destruction of the black. With weak solutions, ten minutes boiling gives a violet-black, which becomes green by action of sulphurous acid.

From the researches of M. Jeanmaire, we know that the ferricyanide of potassium, along with acids, renders aniline black incapable of greening, but this agent making the whites of the cloth blue, led the inventor to the discovery of nitrate of iron as a more practical material for accomplishing the same end.

(f) Persalts of iron in dilute solution.

These salts in the cold immediately transform the blue-black into violet-black.

With weak boiling solutions of persalts of iron a new modification of the black results, which is effected in a few minutes, so completely that it afterwards resists the action of sulphurous acid (Jeanmaire, 1876), but at the same time the white of the cloth is perceptibly changed. The black may be bleached if the ferric salt is less diluted (perchloride of iron at 3° B. This solution gives an ochreous precipitate when heated).

The state of peroxidation of the black resisting greening influences is obtained in various ways, more especially with the agents of the three last groups.

Action of Chlorine and Hypochlorites in Solution.—These oxidizing reagents are chosen as types principally because

they allow experiments to be made at will in either alkaline, neutral, or acid baths, giving in each case the same results in two successive stages.

First Stage—Change of the Ordinary Aniline Black into Violet-Black.—The hue of the aniline blacks varies considerably according to the strength or intensity of the colour, or the duration and temperature of the oxidizing action. Thus, when there is a large amount of the black present on the fibres, as in the case of strong colours upon cotton yarn, the black is changed in a few minutes by the warm reagent, and owing to physical causes acquires a true metallic bronze appearance, with a yellow or greenish chestnut coloured reflection. This bronzing has been for some time past practically accomplished by a few dyers and extensively worked; the bronze appearance of the colour spontaneously disappears in the course of weaving, and by contact with the air and by soaping it changes into a fine and full black. This kind of dyed yarn has been in demand by consumers who rightly considered its appearance as the best guarantee of the excellence of the dyeing. It is now generally produced by the direct action of acid chromates upon aniline salts. We shall see that the permanganates also can yield this bronze black.

The other shades obtained by means of the same agents, vary from violet-black to puce, and even to reddish chocolates; these shades being frequently observed in the course of chloring prints. M. Camille Koechlin remarked some time ago that aniline blacks changed or injured by chloring, but not passing a certain limit of red chocolate colour, slowly and spontaneously returned to their original colour, and more quickly when treated with acids such as acetic acid.

It is a general rule that the transformations of aniline black by any kind of peroxidation cannot take place when the oxidizing baths are too strongly acid, for strong acids destroy the first state of peroxidation, which we call the violet-black.

Second Stage—Decolourizing of the Violet-Black previously produced by Oxidation.—By pushing the oxidizing action further the aniline black is gradually destroyed, giving rise to

brown colours, or the Bismarck shade, or buff colours of varying intensity, frequently with the formation of tarry and pitchy substances adhering to the fingers, particularly observable in moist samples treated by chlorinated gases. These residuums of oxidation, which deserve studying, consist of brown matters very soluble in alcohol, ether, and benzine. They dye silk without mordants, giving browns of an orange hue which can be again dissolved out by alcohol.

In every case of the action of hypochlorites upon aniline black there may be constantly remarked from the commencement to the end of the reaction a characteristic feeble aromatic odour, which recalls to the mind that of aniseed, or to some degree that of gillyflower. This smell remains after all the washings, and even after drying in the air, but it is instantly dissipated by steam. In chloring aniline blacks on the print-works this smell can be sometimes observed more than a hundred yards away from the apparatus.

The alkaline hypochlorites in warm and strong baths can also serve, as I have previously pointed out, to readily determine the comparative fastness and richness of the aniline blacks which is the most resistant, and consequently the most useful of the compounds formed by the artificial alkaloïds; if the action be prolonged for a sufficient time upon various printed specimens they will be found to shew distinct differences of colour.

The decolourization of the aniline black under certain conditions by means of chloric acid, chromic acid, and permanganic acid has been studied previously, and the records are to be found in the Bulletin of the Society.

It is interesting to observe that the oxygenated compounds of chlorine which stand below chloric acid, and which so readily give rise to the formation of aniline black, are precisely those which conduce to its most complete destruction. Chloric acid, or a chlorate with addition of hydrochloric acid, in presence of a small quantity of a salt of vanadium, produce a perfect white discharge.

A simple and conclusive experiment may be made to illustrate this point. Let bands of calico be steeped in solu-

tions of muriate of aniline of various strengths, from 1 to 200 to 1 to 20, and, after drying, spotted over with a solution containing 5 per cent of chlorate of potash, with a quantity of vanadium equal to a thousandth part of the chlorate, the chlorate solution being acidulated with various amounts of hydrochloric acid. By leaving the calico in air at about 60° or 70° F., the spots will be found in the course of an hour to be uniformly green, then the centres change colour, becoming more rapidly bleached as the chloride has been more strongly acidulated to commence with, until after a few hours there is nothing left but wide rings, black and violet-grey at the outside, diminishing in colour even to white at the centres, following certain zones where the chloric acid has predominated more or less over the aniline.

The muriates of pseudotoluidine and xylidine give blue-greys, which are more easily discharged than the aniline grey, and which, by neutralisation, tend towards violet. The muriate of toluidine in the same way yields browns. Yellow cubical catechu gives colours which at first become darker, and then also becomes lighter from the centre.

If the calico experimented upon has been previously dyed in indigo blue, or in ordinary aniline grey, or ungreenable aniline black, all these colours disappear in their turn with strongly acid solutions, but the discharging effect is less perfect at the centre of the spots upon the dyed calico, in proportion as there exists at the same time upon the cloth another substance, soluble and oxidizable, such as the muriate of aniline, upon which the oxidizing action spends itself.

Action of Nitrites.—A one per cent. solution of nitrite of soda, made neutral by nitric acid, acts slowly in the cold upon the ordinary black and grey, simply washed off, changing them at first to a green-blue, but does not change the violet-black resulting from treatment with bichromate; gradually the shades become grey-violet and even rusty-violet, and, as with the alkaline hypochlorites, the colours eventually become brown or buff. By heating the same result is obtained, but more quickly.

In both cases, however, it may be observed that the greys

which are at the maximum of oxidation are but slightly attacked. Further, the blacks are never at any stage changed into the ungreenable black, even when the nitrites are more concentrated, or if they are so acid as to bleach the colour, or if boiled a long time with the colour. Nitrite of soda, 10 per cent. solution, with an excess of free soda, does not act in the cold; about 160° F. the blue-black becomes more intense, and approaches the violet-black, but when the boiling point is reached the shade approaches the primitive blue-black; an effect which must be attributed to the influence of the caustic soda.

All the nitrites are decomposed by acids, and the nitrous gas set at liberty is destroyed by the water, with formation of the bioxide of nitrogen and nitric acid, therefore free nitrous acid does not exist. This instability of what may be called the nitrous anhydride endows it with energetic oxidizing powers.

On account of these properties, it can be understood that the methyl-aniline violet cannot serve to indicate the neutrality of the nitrites of the alkalies. When the violet reagent is brought to a deep green, by a trace of nitric acid, and then a nitrite, with an excess of alkali added, a grey-blue colour is obtained with a partial precipitation of the colouring matter, which does not become red-violet.

Nitrous Sulphuric Acid.—This liquid which is a commercial article marking $67\frac{1}{2}^{\circ}$ B., is sulphuric acid saturated with nitrous vapours, and was recommended in 1876 for use in preventing the greening of blacks. When dissolved in a large quantity of water and partially saturated by adding twice its weight of crystals of carbonate of soda, it should be for experiment diluted finally with five hundred or one thousand times its volume of water.

In the cold, aniline greys and blacks change to green-blue in this acid; by heating, the shades go to violet-grey, the maximum of action appearing to be effected at about 180° F. rather than at the boil. After washing, the greening influence of sulphurous acid is found to be notably less than before, but the preservative action of the persalts of iron or boiling chromic acid is much more complete.

When the bath is not so diluted its acidity interferes with the oxidizing power of the nitrous compound, at the same time it destroys grey colours which have been already changed.

Peroxide of Hydrogen.—In a dilute state, containing four or five times its volume of oxygen, heated with the blue-black it changes into violet-black without decolourizing, much oxygen being disengaged. The addition of a small quantity of hydrochloric acid to the same solution of peroxide of hydrogen, and heating to boiling disengages very little gas and turns the black to blue-green, which becomes violet-black in alkali. There is a slow decolourization, but the maximum of oxidation which gives the ungreenable black is never attained. This black is scarcely acted upon by the peroxide of hydrogen, although so easily influenced by the oxygenating bodies which contributed to its formation.

At the same degree of dilution the acidulated peroxide of hydrogen in the cold and with several hours of contact does not colour solution of muriate of aniline; by heating, it forms dark green flakes which assume the characteristic violet-black colour with alkalis.

Diluted peroxide of hydrogen can then give rise to aniline black by acting upon muriate of aniline, but it cannot change it into the non-greening variety.

Action of Permanganates and Bivanadates.—Neutral or alkaline permanganate of potash in the cold immediately produces the violet-black, and if the black be in sufficient quantity the chocolate bronze appearance previously noted; if the permanganate be concentrated it decolourizes the black in a short time, but neither permanganate alone nor with the addition of sulphuric acid can bring the black into that state where it becomes invulnerable to the action of sulphurous acid, not even by heating or prolonging the action. The latter remarks shew the essential conditions as we shall see whatever method of oxidation may be used. It appears that to succeed the solution should be always so dilute as not to induce a too rapid destruction of the aniline black instead of the slow action desired. The *bivanadate of ammonia* in 1 per

cent. solution has no action upon either the aniline blue-black or grey.

The same solution acidified with hydrochloric acid decolourizes the black at the boiling point, but does not change it in the same manner as chromic acid.

Arsenic Acid.—Arsenic acid in 5 per cent. solution acts only upon the aniline black and greys as a moderately strong acid, even when heated to the boiling point.

Action of Chromic Acid and Acid Chromates.—We will endeavour to add some facts to the numerous researches which have been made upon the use of the soluble chromates, because they include some points which have hitherto appeared to be contradictory.

Neutral chromate of potash does not act upon the blue-black; neither does the chromate of potash made alkaline. In both cases the after treatment by acids after washing, and then by alkalis, shews that there has been no oxidation, the black remains blue-black.

The oxidizing influence of chromic acid upon the ordinary aniline black is characteristic, and varies according as this acid is free or combined in some of its different compounds. The neutral chromates of potash and soda, etc., have not, I repeat, any action; but if to their aqueous solution a small quantity of any strong acid be added so as to give rise to the formation of a portion of bichromate, even when some neutral chromate still remains, the blue-black changes to violet-black, and becomes then more capable of resisting greening influences, they are, as it is known, retarded. For this reason, as much as to be assured of the complete oxidation of the aniline in printed blacks, the use of bichromate of potash, either cold or warm, had been recommended from the beginning by those who had worked upon this colour. The advantages of the use of this oxidizing salt had been clearly described and pointed out by M. F. Lamy in several communications upon the greening of aniline black.

If the quantity of acid added to a chromate exceeds that which is necessary to convert it into bichromate, so that a portion of chromic acid is set at liberty, quite different results

are obtained. I have found that a solution of bichromate containing $\frac{1}{2}$ or 1 per cent. of salt, does not prevent the greening of the black by sulphurous acid in the least, after ten minutes boiling with it. The same solutions of bichromate acidulated with 1 per cent. of strong sulphuric acid will prevent greening after three minutes' boiling, though it partly decolourises the black.

Free chromic acid has therefore an action perfectly distinct in this case from bichromate of potash, and this is not the only case in which a difference may be observed in its action upon colouring matters. With 1 part of crystallized chromic acid to 1000 parts of water, boiling for half a minute produces a change in the black; with about six minutes' boiling it has become insensible to the action of sulphurous acid. M. Lamy was led to advise the use of hydrofluosilicic acid along with bichromate of potash to liberate the chromic acid from the potash.

The following results were obtained by experimenting upon small parcels of aniline grey and black, keeping them uniformly for *ten minutes at the boiling point*, correcting the loss by evaporation:—

Bichromate of potash, 1 per cent. solution in distilled water; the change did not take place. It is important to notice this, because the colours were completely turned green by sulphurous acid, notwithstanding the boiling in the bichromate solution.

Bichromate, at $\frac{1}{2}$ per cent., plus half per thousand of strong sulphuric acid; the colours were strongly acted upon, and did not become green with sulphurous acid.

By replacing the sulphuric acid of the above experiment with equivalent quantities of nitric acid, chloric acid, and hydrochloric acid, the action in each case was more energetic than with sulphuric acid, the black being partially destroyed. It may be estimated from these experiments, that hydrochloric acid acts nearly twice as powerfully as sulphuric acid. This is not surprising, since the acids just named are mono-basic acids, while sulphuric acid is bi-basic, the same as chromic acid. Two equivalents instead of one ought to be

required to produce the same state of chemical equilibrium amongst the substances present in solution.

By replacing, in the same way, the sulphuric acid by oxalic acid, a more powerful action is observed, the shades turn to pink-grey, and are not changed by sulphurous acid. The solution, diluted with an equal volume of water, gave nearly the same results as the original sulphuric acid mixture, but further dilution of the liquids shews very little difference between the action of the two acids.

Again, replacing the sulphuric acid by an equivalent amount of hydrofluosilicic acid, the action was found less energetic than with sulphuric acid; the colours did not become green with sulphurous acid.

The use of acetic acid and salammoniac, instead of sulphuric acid, did not give any action.

Replacing the sulphuric acid by pure sulphate of alumina, reckoning three equivalents of combined acid as equal to one of free, produced very little effect.

Lastly, the solution of bichromate being mixed with perchloride of iron, without any excess of acid, completely prevented the greening as the iron salt does alone. Oxide of iron was deposited upon the cloth. Continuing to use, as a fixed quantity, an amount of hydrochloric acid, equivalent to half a part of sulphuric acid per thousand of water (0.5 grammes concentrated acid per litre of water), and progressively diminishing the proportions of bichromate of potash for the experiments which follow: it was found that it might be brought as low as between $2\frac{1}{2}$ and $1\frac{1}{2}$ parts per thousand of water, still obtaining the same results, beyond that point the differences were more noticeable. For the following experiments the strength used was $1\frac{1}{2}$ per thousand. The addition of an alkaline chloride, such as chloride of sodium, with the intention of raising the boiling point, did not appear to be favourable.

[The table which follows shews in a more condensed form the appearances and behaviour of the black at various stages with reagents.]

<i>Different stages of oxidation of the Aniline Black produced by means of Chlorates.</i>	<i>Names used and employed, with their principal characters.</i>
<p>(1) Development of the colour; weak colour or incompletely oxidized and of small depth; produced cold or warm in weak solutions or mixtures.</p>	<p>Formerly called emeraldine, or azurine. This colour is a very weak aniline black, or rather a blue-grey when it is neutralized. In the acid state it resembles emerald green. In both states it is extremely sensitive to reagents.</p>
<p>(2) Complete or finished black, sufficiently dense at the maximum of oxidation obtainable by chlorates at temperatures between 70° and 100° F.</p>	<p>This is the ordinary aniline black called BLUE-BLACK, such as it was generally produced by printers from the commencement until 1876 or 1877. In the acid state this black is green, its depth depending on its concentration, in other respects it is the same as the above.</p>
<p>(3) Finished black, with an additional oxidation by various agents, neutral or acid, but in the cold or below 158° or 167° F. The very deep black has an inclination to a bronze upon yarn. The effect of this partial oxidation is destroyed by prolonged contact with strong acids.</p>	<p>Oxidized aniline black called VIOLET-BLACK. It is obtained from the preceding colours, generally by treatment with acid chromates at a temperature below 167° F., or else by insufficient time in boiling solution. The shade is a fine violet-black after neutralization. The greening is retarded.</p>
<p>(4) Finished black, with a slow and hot oxidation between 170° and 212° F. pushed to the maximum during a space of time sufficient to render the black ungreenable.— It is observable that upon calico this black is wetted with difficulty, which is owing to incipient destruction by peroxidation. It cannot be brought to the condition of the blue-black.</p>	<p>Peroxidized aniline black called the ungreenable black. Beautiful and intense colour, sometimes with a reddish or foxy cast; very little acted upon by acids, and especially by sulphurous acid and sulphuretted hydrogen, but has become more easily attacked by hypochlorites, etc.</p>
<p>(5) Destruction of the black caused by excess of oxidation. The cellulose itself beginning to be acted upon; the black now incapable of being restored.</p>	<p>The black gives place to oxidation products of ochrey, rusty, and yellowish colours, becoming weaker and weaker, forming a tarry substance insoluble in water, acids, or alkalies, and upon which chemical agents have scarcely any action.</p>

<i>Appearances after washing in the neutral or alkaline state.*</i>	<i>Action of strong acids diluted with water.</i>	<i>Action of sulphurous acid even when very weak.</i>
<p>blue grey.</p> <p>With aniline in excess = 5 blue $\frac{1}{10}$ black becoming when 1 violet-blue $\frac{1}{10}$ black; with rate in excess violet-blue black.</p>	<p>Emerald green of dark shade.</p> <p>= 1 green $\frac{2}{10}$ or $\frac{1}{10}$ black.</p> <p>= 1 green $\frac{0}{10}$ black.</p>	<p>Yellowish green.</p> <p>= 2 green-yellow $\frac{1}{10}$ black.</p> <p>= green-yellow $\frac{0}{10}$ black.</p>
<p>black, with blue shade.</p> <p>as above with greater depth.</p>	<p>Dark green.</p>	<p>Yellowish-green more or less deep.</p>
<p>tense black with violet shade.</p> <p>to aniline in excess = violet-$\frac{1}{10}$ black, and when dry 2 violet-blue $\frac{1}{10}$ black.</p> <p>with chlorate in excess 1 violet $\frac{1}{10}$ black.</p>	<p>Dark green.</p> <p>= 1 or 2 green $\frac{0}{10}$ black.</p> <p>= blue-green $\frac{7}{10}$ black.</p>	<p>Yellowish-green deeper than the above.</p> <p>= 2 yellow-green $\frac{1}{10}$ black.</p> <p>= 1 yellow-green $\frac{0}{10}$ black.</p>
<p>well saturated fine black, or to dilute a clear grey.</p>	<p>Black, shewing green tinge upon the ends of threads.</p>	<p>Pure black, perhaps slightly olive at the ends of threads.</p>
<p>chre-brown, or fawn shades becoming gradually weaker.</p>	<p>Browns faintly greenish. Towards orange $\frac{7}{10}$ black.</p>	<p>Browns faintly greenish.</p>

The shades are designated according to the nomenclature of Chevreul's chromatic circle.

Again, taking a solution of bichromate of potash, containing two of salt per thousand of water as a standard, and diminishing the hydrochloric acid so as to be equivalent to 0.5, 0.4, and 0.3 per thousand; the inattackable black was constantly obtained.

With bichromate at 1 part per 1,000 of water, and the hydrochloric acid equivalent to 0.4, 0.25, and 0.2 of sulphuric acid per 1,000, it was found that the two last did not influence the black so as to enable it to resist sulphurous acid.

It is evident from this that in weak liquids (1 of bichromate per 1,000 of water) that the hydrochloric acid must be in equivalent quantities to produce the desired effect, but in stronger solutions (2 to 5 per 1,000) less than an equivalent of acid acts powerfully in preventing the greening of the black, although it is demonstrated that bichromate of potash without acid has no action; the nature of the decomposition of the salt must then be somewhat different according to the degree of concentration. Hydrochloric acid employed along with bichromate in proper quantities has given me excellent results on the large scale, a fine black with very little injury to the white cloth.

It is well, however, not to raise the proportion of acid too high on account of the whites. Thus when sulphuric acid is used in slight excess, that is when more than 4 lb. of the concentrated acid is used to 10 lb. bichromate in solutions containing 2 or 3 of salt per 1,000 of water, it is observed that the whites became tinged brown, and this tinge is difficult to remove by boiling lime water or hypochlorites; a small excess of bichromate is therefore to be preferred.

It will be observed that to obtain the special modification of aniline black not liable to green by the action of sulphurous acid, the ordinary means of oxidation were for a long time insufficient, this was because it was absolutely necessary to unite in one process several special conditions, one or other of which were wanting in all the processes used. These conditions are:—

(1) Oxidation in an acid medium. This alone is insuf-

ficient, the single example of permanganic acid shews that no complete results can be obtained by it.

(2) Slowness of oxidation. What is required is a moderate and progressive oxidation; it is easy to conceive that a sudden action would destroy a portion of the insoluble black before being able to act efficaciously on the whole.

(3) An elevated temperature. The transformation of the black hardly takes place lower than 212° F.; at 176° F. it is much less complete. It is necessary to take advantage of the temperature to determine a weak action which presents the oxygen in a nascent state. There are very few cases of oxidation where the ungreenable modification is obtained at a low temperature (ozone air, oxides of chlorine.)

An oxidation which is at the same time acid, slow, and at a high temperature definitely modifies the finished aniline black, and renders it invulnerable to sulphurous acid; this operation consequently protects the black against nearly all further spontaneous injury from action of the air, which was the only weakness of the splendid colour.

Reducing Agents upon Aniline Black.—None of the various reducing agents in the moist way, or more correctly speaking, none of the hydrogenizing chemical reagents can in any degree bring back the peroxidized aniline black or the ungreenable black, into a state corresponding with the original blue-black; the intermediate violet-black is much less stable, and it submits to this change under several treatments. We have already seen that this change is effected by simple contact with moderately concentrated hydrochloric acid, but in alkaline liquids it is realized without difficulty and by a great number of substances.

With sufficiently powerful reducing agents, properly chosen, the shades of the various aniline blacks, including the black at the maximum of peroxidation, are successively modified into yellowish green and olive when the solutions are acid, and into a bluish grey when they are alkaline, and finally, always into a very pale brown or buff as the last stage. There is

probably formation of several hydrurets, and the insolubility in acids or alkalies is a constant feature, but we may remark that in most cases the feeblest oxidizing influence re-establishes afterwards respectively the blue-black and the peroxidized black, such as they existed at the commencement. These two states of the aniline black are therefore completely distinct in their fundamental characters; their apparent analogy during decolourization by hydrogenation is but of a momentary nature.

Sulphurous acid, sulphydric acid, and the sulphhydrates, which have no action upon the peroxidized black, immediately change the ordinary black to a greenish yellow or pale olive, appearing to contract special combinations which oxidizing agents easily destroy.

We shall commence by examining, one by one, each of the last series of facts, and we shall classify as much as possible the succeeding reducing actions into those effected in an alkaline, and those effected in an acid medium.

Action of Sulphurous Acid.—The action of this acid deserves to be first considered, on account of its activity as compared with other acids, as well as the peculiar action which it exercises upon certain colouring matters.

Sulphurous acid, in aqueous solution, strongly reddens litmus; it is bibasic, and in combining with alkalies it forms:

(1) Salts which, in a state of purity, are neutral to litmus—the bisulphites. These salts have a tendency to disengage sulphurous acid at the ordinary temperature. Now as it is known sulphurous acid, in contact with water, is readily oxidized in the air, and more especially in the light, the bisulphites, therefore, soon contain sulphuric acid, which causes a further disengagement of sulphurous acid, and then it reddens litmus, which is ordinarily the case in solutions of this salt.

(2) Sulphites, on the contrary, have an alkaline action upon litmus. When litmus is reddened by sulphurous acid its colour is weakened, and at length disappears when the liquid is completely shut off from the air; it recovers its colour immediately when treated by sulphuric acid, which, being a

stronger acid, expels the sulphurous. The same thing takes place when the solution is carefully treated with chlorine, which converts the sulphurous into sulphuric acid. We believe that sulphurous acid behaves in a similar way with aniline black, although the black never loses its colour completely.

Sulphurous acid and the bisulphites do not change the violet reagent (*Violet de Paris*). The mode of action of sulphurous acid appears, as far as regards acidity, to be the same as the weak acids, of which acetic acid and the biacetates are types, with this difference, however, that the methylaniline violet is immediately bleached in cases where the colour of litmus is only weakened.

With methylaniline violet the effect cannot be well seen except by adding drops of it upon the liquid, in the reverse way the colour disappears too rapidly for observation; there remains, however, a trace of coloured substance in suspension, forming a sort of reddish fluorescence, which passes, after a little time, when the violet is completely destroyed.

The weaker acids themselves have an evident action upon ordinary aniline black, blue-black, and violet-black, although they cannot change the shade of the aniline violet; such, for example, is the case with acetic acid as well as sulphurous acid.

Sulphurous acid has also a secondary chemical property of changing the blue-black and the violet-black to a characteristic yellowish green shade, distinct from that produced by other acids. This action, which I believe to be wrongly considered as one of reduction, is better viewed as the result of a simple combination of sulphurous acid with the non-oxygenated bases, which constitute the phenylamine black, having analogy with the known action of sulphurous acid upon several organic colouring matters. In these cases strong acids have a tendency to displace the sulphurous acid from its combination; and the same thing takes place with the aniline black brought to the yellowish green state. Suitable oxidizing agents easily destroy the sulphurous acid, at the same time annulling the changes of colour produced by this body, just the same as with other colouring matters.

A concentrated solution of an alkaline sulphite, containing a small excess of alkali, is without action upon aniline black or grey in the blue-black state. Thus, after washing, hydrochloric acid only changes these specimens into a more or less dark greenish blue; while the same colours, which have been first greened by sulphite (not alkaline) and then brought to the grey-blue by caustic alkali, take, after well washing, the yellowish green colour characteristic of sulphurous acid by the slightest contact with dilute hydrochloric acid. This fact is of itself sufficient to demonstrate that there exists, at least, a momentary but real combination between sulphurous acid and ordinary aniline black.

An aqueous solution of sulphurous acid, or a mixture of bisulphite of soda with a little hydrochloric acid, and much diluted with water, forms the best test liquor for testing the state of peroxidation of aniline black, or in other words, the degree of resistance of various aniline blacks to those atmospheric influences which produce greening. This liquid should be kept in a well stoppered bottle, and in a dark place.

To test various black colours nothing more is required than to place a thin layer of the testing liquid upon a white plate and add bits of the coloured cloths; it is best to tear, and not to cut with scissors, the bits to be tested, for then the fine fringe of the torn filaments which project allow the slightest variations of colour to be seen against the white ground of the plate.

As to spontaneous greening, it is most marked in moist air, and during the existance of fog and mist in cold weather. It takes place both in open and closed places, where illuminating gas is burned, or where coke and coal are used for fuel, that is where sulphurous gases exist, and is perceived on the folds where vapour condenses, and also in dew and hoar frost. However little sulphurous acid may be in the air it is rapidly concentrated upon a small surface of the cloth, which readily absorbs humidity, and the black in those places is liable to become green in a very short time.

Hyposulphites.—Hyposulphite of soda, even at the boiling point, has no action whatever upon the different aniline blacks in the neutral state. The addition of the smallest quantity of free acid will, of course, give rise to the reaction of sulphurous acid.

Action of Sulphydic Acid (Sulphuretted Hydrogen.)—An aqueous solution, freshly prepared, of sulphuretted hydrogen, which faintly reddens litmus, acts strongly upon aniline greys in a few seconds reducing their colour, and changes blacks, chromed or not, into an olive colour of greater or less intensity. Sulphuretted hydrogen has no action whatever upon the same colours which have been previously brought to the degree of peroxidation where they are ungreenable; the difference being of the same kind and as distinct with sulphuretted hydrogen as with sulphurous acid.

The colours thus affected by sulphuretted hydrogen when exposed to the air change slowly to blue-green, and are rapidly brought to the same colour by oxidizing agents. The violet-black arising from the action of bichromates is brought to the state of blue-black.

A solution of colourless *mono-sulphide of sodium* with an excess of caustic soda has very little action in the cold upon washed-off blacks and greys, whether chromed or not. When it is very carefully neutralized by hydrochloric acid, all the colours become paler, but they are restored somewhat by washing. When examined in the moist state the blacks appear greened, the greys, whether chromed or not, are rather olive, and change after a while to green-blue; the blacks and greys at the maximum of peroxidation are scarcely changed; the violet-black appears to be destroyed.

With an excess of hydrochloric acid, and if hyposulphite exists in the liquid, there is a white precipitate, and the liquid has the reaction of sulphurous acid.

A solution of *yellow sulphide of ammonium*, such as is ordinarily used in laboratories, diluted with ten times its volume of water acts in three minutes, precisely as the

mono-sulphide of sodium neutralized, but more quickly and more completely; that is, the grey becomes and remains colourless as long as it is in the solution.

The same liquor neutralized by hydrochloric acid strongly reduces the colours above and changes ordinary black to a dark olive; the black at the maximum of oxidation is not changed. After washing and drying in the air the yellow-green is obtained as with sulphurous acid; the violet-black produced by chroming always takes a more yellow shade of green, but it is destroyed, as is easily shewn, by treatment with first weak acid and afterwards by alkali. It follows from the above experiments:—

(1) That sulphuretted hydrogen changes various finished aniline greys and blacks, and especially emeraldine, to an olive shade. Emeraldine remains insoluble, same as other colours of the same origin. In sulphuretted hydrogen and the sulphhydrates (although the contrary was published in 1876), those agents which expel or destroy the sulphuretted hydrogen, restore the colours immediately.

(2) The simple treatment of the black with bichromate of potash even at the boiling point does not preserve it against the influence of sulphuretted hydrogen; the special action which the bichromate has upon the black is even neutralized.

(3) The peroxidation of the black by boiling chromic acid renders the colours absolutely invulnerable to sulphuretted hydrogen.

Action of Hydrosulphites.—The hydrosulphite prepared with bisulphite of soda at 35° or 40° B. in contact with metallic zinc for twenty minutes warm, then diluted with ten or more times its bulk of water, decolourizes energetically all the aniline blacks in the cold, and still more rapidly when warm. The action is slower but precisely the same when an excess of caustic soda is added to the hydrosulphite; it is complete in a few hours, and shews no further change after an interval of thirty hours. In all these cases the aniline greys and blacks become nearly colourless or of a pale fawn shade, and are excessively prone to absorb oxygen, and then return

to their original shades, possessing the same properties as before. In this decolourized state the changed black remains completely insoluble in either acids or alkalies. In this respect there exists an essential difference between them and the aniline greys and blacks lately obtained by M. Goppelsroeder by reducing the sulpho-acids of aniline black with glucose, since the latter reduced substances are soluble.

The colours which have been rendered ungreenable by the process of peroxidation are temporarily bleached like the others, but when exposed to the air they resume their primitive appearance, and their insensibility to the action of sulphurous acid and sulphuretted hydrogen.

After the *acid* hydrosulphite the blacks, washed in distilled water and dried slowly in the air, shew the same shades of yellow-green that they do with sulphurous acid, without change of intensity. The grey and violet-black, produced by bichromate, give only a green slightly more yellow than with the blue-black, a character which is generally observable. By treating the specimens afterwards with weak caustic soda the grey-blue is reproduced, and there is then no difference between the blacks which had been treated with bichrome or those simply washed off.

After the *alkaline* hyposulphite the blacks, washed and exposed to the air, are restored to the blue-black, identical with the colour washed off in alkali, and of precisely their original shade. The violet-black, derived from the bichromate treatment, is found brought to the state of blue-black.

The white of the cloth is not tinged by these various treatments in the reduction of the blacks.

The most striking point in these experiments is that notwithstanding the temporary decolourization, induced by the hydrosulphites, upon the peroxidized black, it retains its permanence after revival. The following experiment suffices to make this clear:—

All kinds of aniline blacks and greys when treated with acid hydrosulphite of soda and zinc, either hot or cold, remain insoluble, but are reduced to a pale buff tint; in this stage it is impossible to distinguish one from another. The

action of the oxygen of the air, or of aërated water, by destroying the effect of the hydrosulphurous acid, rapidly restores the colours to their original state, both as regards shade of colour and their other properties.

The restoration of the colour can be hastened, after washing, by passing the cloth into a solution of sulphate of copper at $1\frac{1}{2}^{\circ}$ Tw.

Tested afterwards by sulphurous acid the ungreenable blacks change to grey, more or less reddish, while all the others are yellow-green. The contrast of the extreme specimens is very striking, but these and the intermediate ones behave identically as they did before being subjected to the action of the hydrosulphite.

A remarkable fact is that the hydrosulphites appear to yield more hydrogen to the blacks than is actually required to reduce the colour to the extent stated above, thus, when the washed specimens are exposed to the air the blacks are seen to be slower in developing just in proportion as the hydrosulphite has been used stronger, or the time of its action prolonged. With an equal amount of hydrogenation the greys and blacks which have been peroxidized recover their colour first.

Alkaline Reducing Agents.—Pure caustic soda somewhat concentrated in the cold, and when hot diluted, slowly destroys the violet-black produced by the bichromates, and appears at first to give a greater intensity to the blue-black, so that there is less difference between the two shades. With boiling alkaline solutions all secondary action which may take place from the remains of starchy matters from the thickening must be carefully guarded against; these matters can only be removed by frequent and prolonged macerations at 100° F., in decoction of malt, followed by washing and boiling in soap.

Even after having taken all precautions in this way, it is seen that after a few minutes' boiling in caustic soda, light greys of different qualities become weaker, but recover themselves almost completely by exposure to air; the intermediate violet-black is changed to blue-black. The liquid becomes violet coloured, which colour it loses upon addition of acetic

acid. Caustic soda at 3° to 6° B., with 1 per cent. potato starch, causes the loss of colour of dark aniline greys, in a few moments boiling, down to a very pale buff, and peroxidized black to a light fawn; the blue-black resists longer. The caustic itself acquires only a light reddish or violet colour. As soon as the colours are exposed to the air, or better still, when the liquor cools down sufficiently for the air to penetrate it, the colours become gradually darker until they have attained their original state, without any change in their properties.

When not more than one-thousandth part of potato starch is present in caustic soda at 3° B., the temporary decolouration of the grey takes place in three or four minutes' boiling. The action is less vigorous with more diluted soda.

After many other neutral soluble organic substances had been tried, principally of that class looked upon as hydrates of carbon, the above phenomena appeared general. Alkalies in solution tend to oxidize these substances, while presenting nascent hydrogen to the aniline blacks, which decolourizes them. The conversion of indigotine into indigo-white in hot alkaline solutions under the influence of pectine, as in Leuchs' process, is analogous and typical of these reactions. The decolourizing of aniline black is effected under the same circumstances quite as easily as the reducing of indigo. That it has not hitherto been noticed in the numerous cases where it may have taken place, must be attributed to the fact that the regeneration of the colour is nearly complete, and is effected so rapidly that the change would easily escape observation.

By heating the various aniline blacks with caustic soda containing glucose, when the temperature reaches 160° F. the greys and blacks lose colour, and in two minutes' boiling are brought down to the fawn shade, while the liquor becomes brown. In the course of washing, the colours revive with great rapidity, losing without doubt the hydrogen with which they had combined, it forming water with the oxygen of the air. It is the blue-black which is reproduced, while the violet-

black is destroyed. As to the ungreenable blacks, when they are revived, they are still as before, invulnerable to sulphurous acids, etc., but the other blacks behave as at the first.

Clear lime water heated to boiling with specimens of printed aniline grey quite free from thickening acts by bringing them immediately into the blue-black state of the grey, when they had previously been in the corresponding violet-black state; after a few minutes it has a temporary decolourizing influence upon the greys at the maximum of oxidation.

An addition of $\frac{1}{200}$ of cane sugar to the boiling lime water gives it a more decided decolourizing influence upon the different aniline greys. The same takes place with caustic soda.

For the following experiments the alkaline solution was boiling, and contained $\frac{1}{4}$ equivalent of caustic soda per litre :—

With the addition of one-thousandth of wheaten starch it decolourizes aniline grey as well as with the same proportion of potato starch. The caustic does not become coloured.

Gum arabic, $\frac{1}{200}$ part also decolourizes it; the liquor becomes yellow. With a thousandth part of *gélöse* or *Hai-thao*, or with the same quantity of *dextrine*, the action is much more powerful. Medium greys are completely decolourized by three or four minutes' boiling.

Milk sugar appears to possess the most powerful action, $\frac{1}{2000}$ part suffices to produce the decolourization of the grey in a few minutes.

Glucose resembles the preceding in its action, though it is less quick than an equal weight of milk sugar. The liquor becomes first yellow, then brown by heating.

Amongst other organic matters the following in the quantities set down produce an equal action with boiling caustic soda :— $\frac{1}{100}$ of pure *glycerine*, $\frac{1}{200}$ egg *albumen*, $\frac{1}{200}$ pure *tannic acid*, $\frac{1}{200}$ *gallic acid*, $\frac{1}{1000}$ *pyrogallic acid*; with pyrogallic acid the action commences in the cold. With $\frac{1}{200}$ of *rosin* the decolouration of the grey is nearly completed at the beginning

of the ebullition, but it is doubtless owing to the presence of some foreign matter and not to the rosin, for the action does not continue, and the colours at first reduced are revived even in the boiling liquor.

It is the same with $\frac{1}{300}$ of *gum senegal*.

Gelatine, white Marseilles soap, *aniline*, and essence of *turpentine* shewed no action in these experiments.

By adding the following substances to boiling caustic soda no action was observed, viz.:—*amylic alcohol*, *phenic acid*, *acetate of soda*, *formate of soda*, and *ferrocyanide of potassium*.

Caustic soda at 1 equivalent per litre at the the boiling point with *zinc* powder or with *sulphuret of arsenic*, decolourizes temporarily the various aniline blacks.

The same solution of soda with 5 per cent. of stannous chloride reduces aniline blacks very powerfully, bringing them to the fawn and buff shades produced by the hydrosulphites; at the boiling point the action is very rapid. There exists a remarkable analogy between the results obtained by these various ways. In every case the colours are equally ready to absorb oxygen and recover their original shades. The violet-black is destroyed, while on the other hand the peroxidized greys and blacks are reproduced without change, and enjoying all their characters same as after the action of the hydrosulphites.

In the course of spontaneous oxidation, it is observable that the ungreenable greys and blacks in general, are more quickly revived than the others.

As an application directly flowing from the part of this investigation, which concerns the alkaline reducing actions, there may be mentioned the easy change of the bronze-black of dyed yarn into the so-called black-black or blue-black so much in request for woven goods. The practical interest which this question always has is greater at present because the majority of dyers effect the change of the aniline by means of bichromate of potash and hydrochloric acid, and generally produce the bronze-black. To transform this colour to the pure blue-black shade nothing more is necessary

than to pass the goods for a few minutes, at a temperature between 190° and 212° F., into a caustic soda bath, at 3½° Tw., containing about half per cent. of glucose.

Other Reducing Agents.—A mixture of glycerine, carbonate of soda, and hydrate of stannous oxide, heated to about 250° F., forms a liquid which becomes very alkaline, and which possesses a hydrogenizing action. It decolourizes indigo, as M. Prudhomme has recently shewn, but it still more easily acts upon aniline greys and blacks at their maximum state of oxidation than upon blue-black. After washing, the different aniline greys and blacks, which are reduced to a uniform pale brown, are generally restored to the precise state they were in previously; nothing is dissolved during the treatment, and the ungreenable colours still preserve their properties.

When on the contrary, stannous chloride is employed in feebly acid solution, the same action is observed in the cold as with sulphurous acid; thus the blue-black is changed into yellowish green, while the blacks, at the maximum of peroxidation, resist the action and are ungreenable. By heating, the yellowish green tends to become olive, and the peroxidized grey becomes buff. After washing it is observed that the colours are somewhat changed and lighter.

Very dilute acids, in contact with pure *zinc*, even in powder, do not exercise any particular action upon the greys and blacks, which may be attributed to the insolubility of the active matters.

A solution of ferrous sulphate of iron (protosulphate), at 5 per cent., acidulated with hydrochloric acid gives, in the cold, a yellowish-green colour, analogous to that produced by sulphurous acid, the ungreenable black remaining unchanged. There is no different action upon boiling.

The *Ferrocyanide of Potassium*, acidulated, acts rather more strongly than the ferrous salts, and partially decolourizes the grey; in the air they return to their primitive state. The colours, at the maximum of oxidization, do not undergo any alteration.

Cyanide of Potassium, pure, in 3 per cent. solution, acts only at boiling point and slowly. The ungreenable greys are

those first acted upon, and acquire a pale buff colour, afterwards the other colours are acted upon. After washing, the action of the air quickly restores the greys and ungreenable blacks to their original state.

Arsenite of Soda solution, containing 3 per cent. of arsenious acid, has absolutely no action upon the various aniline blacks and greys, either cold or boiling; the violet-black does not suffer the least change.

Hypophosphite of Soda, with excess of alkali, has no other action than caustic soda; in neutral solutions at 5 per cent., even with boiling, there is no action. Even with the addition of hydrochloric acid nothing peculiar can be remarked. It is, however, known that aqueous solution of hypophosphorus acid is a powerful reducing agent. Thus, by treating the same liquid, below boiling, with sulphate of copper, there is first precipitated hydruret of copper, and lastly metallic copper. This exceptional case is worthy of notice.

To conclude, the detailed examination of the various aniline blacks has shewn that they are much more easily influenced by a great number of reagents, acid, or alkaline, oxidizing or reducing, than was generally thought to be the case; but the black which has been submitted to peroxidizing influences under prescribed conditions, is found to have acquired in a durable manner certain perfectly distinct characters of stability which greatly increase its value.

These investigations are also interesting in so far as they enable the properties of the analogous alkaloids of coal-tar to be compared in similar positions to that of aniline. Notwithstanding all that has been said of the usefulness of the compounds of toluidine, etc.; the aniline black rests unquestionably the most important of all.

I feel pleasure, in conclusion, in acknowledging with thanks the assistance I have received in these researches from my friend M. N. Potier.

Educts from Barwood.—The late Thomas Anderson, M.D., F.R.S.E., has left an account of his researches upon Barwood, which is published in a recent number of the Journal of the Chemical Society. He says Barwood contains at least three colouring matters. Ether dissolves out two of these, and afterwards alcohol dissolves out a third. All are insoluble in benzol, all give puple lakes with acetate of lead and purple colourations with alkalies. Besides the colouring matters, some colourless principles were isolated which, from the botanical name of barwood (*baphia nitida*), have been called Baphum, Baphic acid baphinitin and baphinitone; these substances have only a purely scientific interest.

Rouen Industrial Society.—The Bulletin of this Society for the months of March and April, 1877, besides the articles which we extracted from it in a previous number, has some others of less interest for our readers. There are reports upon a so-called soluble aniline black offered for consumption by M. Collin. M. Glanzmann reports at some length his experiments upon it, but as he quite failed to obtain anything good, it is hardly worth while to follow all the details of his trials. M. Hommey reported upon the same article as regards its applicability to woollen dyeing, but here also the results obtained were unsatisfactory, the black was not good and not fast. According to the manufacturer, the soluble black is a product of the oxidation of aniline by nitro-benzine in presence of an organic acid.

In the same journal there is a description of a patented stretching or widening machine for calicoes, which is reported as possessing some advantages over the existing machines in respect of facility of use, power of control, smallness of space occupied, and lowness of price; its construction, is illustrated by elaborate plates.

2. *Abridgments of Complete Specifications of Patents Recently Published.*

A.D. 1876, October 11th.—No. 3929.

CRAWFORD, WILLIAM. "Improvements in Bleaching, Washing and Dyeing Yarns in Hanks, and in the Machinery or Apparatus employed therefor."

The following is the provisional specification of this patent; the complete specification refers to four figures of the machinery, on one sheet, and is published at 6d.

"This invention has reference to a new or improved mode and means or mechanism for carrying and conveying all kinds of thread or yarn in hanks, such as that of cotton, wool, silk, jute, or other fibrous material, through the liquid, steaming, or other troughs or chambers for treating the same in the process of bleaching, washing, or dyeing, all in a more simple, efficient, and expeditious manner than heretofore.

"And the nature and novelty of the invention consist in mounting two endless webs of network over and between two driving or drawing and nipping rollers at the upper part of one end of the machine driven and geared so as to actuate and draw the webs and yarn through the liquid troughs or other chambers, the one web being carried across from the top roller for a considerable distance nearly horizontally and over a guide roller at the opposite side of the machine; the upper web being carried up over one or more rollers situated above the lower horizontal web, thence on to and over the same guide roller from which both webs undulate round and under a set of rollers at the bottom of the trough or chamber and up over a corresponding intermediate set of rollers at the top thereof, and finally pass out through between the nipping or drawing rollers before referred to, which are fitted in proper bush bearings and standards at the one end of the machine,

where one of the roller spindles may be conveniently driven by belts and pulleys or other ordinary driving gear and fitted with stopping motions, the action of the machine being as follows:—

“The hanks of yarn to be bleached, washed, dyed, or otherwise treated, are spread in an open or other loose manner upon the top of the horizontal travelling web as it travels towards the guide roller, where the upper web then gripes the hanks as the two webs pass over the guide roller and carrying the hanks between them in the up and down, vertical, or other undulating manner, backwards through the troughs or chambers before referred to until they reach and pass through between the drawing rollers where the water or liquid may be pressed out of the hanks, and after passing over the upper roller the hanks are left free on the upper surface of this end of the lower horizontal web ready to be lifted away as the upper web rises over its opening and guiding rollers, leaving the upper surface of the lower web free for the reception of fresh hanks as before described to be carried and treated in like manner through the troughs or machine.

“Although nets have been described for the carrying and griping of the hanks of yarn, it is to be understood that wide meshed wire cloth, or a series of endless bands or cords of wire cloth or other material might be used instead.”

A.D. 1876, October 18th.—No. 4031.

BIRCH, WILLIAM. “Improvements in Squeezing Machines.”
(*This Invention received provisional protection only.*)

“Instead of the expensive sycamore, cotton, rubber, or other flexible rollers used in squeezing machines for bleach works, and the like purposes, I employ metal, being much more durable and cheaper in use; but in order to attain the same conditions, as if the rollers were made of more flexible material, I form one of the two with a groove in the direction of the circumference. In this groove the other flat or male roller fits tightly at the top or edges of the groove; but at the bottom thereof, that is, at the face of the female roller, I allow

a little more room, so as to make the groove wider there, in order that the cloth when it is being carried through the groove and between the rollers may not bind between the sides of the groove and the ends of the female or flat roller, and be cut or torn by the latter.

"When working continuous from the squeezer to the drying or other machine, I do not drive the squeezer direct, but employ a regulating motion of any known construction, a pair of conical drums with a strap shifting arrangement being found convenient. In such a case the cloth passes through a pot eye at the end of a bell-crank lever, and when the drying or other machine is standing and takes no cloth, the bell-crank will hold the strap fork on the loose pulley at the end of one of the drums; but if the drying or other machine is started and requires cloth, the strain on the same through the pot eye on the bell-crank will shift the strap on to the drum, and in such a position on the same as to drive the squeezer at the exact speed at which the cloth is taken by the following machine.

"Important points in this invention are,—

"The slight conicity given to the groove of the roller, by the adoption of which the arrangement becomes alone practical and useful.

"Also the application of a regulating motion to the driving of the squeezer, as described, or other similar machinery; and, further, these improvements when applied either singly or combined."

A.D. 1876, November 28th.—No. 4598.

COOPER, FREDERICK. "Improvements in the Construction of Apparatus Employed for Finishing Velvets and Velveteens and other similar Piled Fabrics."

"This invention relates to the ordinary machines employed for finishing or 'pegging' velvets, velveteens, and other similar piled fabrics, the object of the invention being to enable such to finish the fabrics up to the front end of the piece, or nearly so, instead of leaving about a yard unfinished which required to be afterwards finished by hand as usually practised.

“In place of the ordinary plain tension roller close to the lower end of the ‘finishing-plate’ in such machine, I mount a roller covered with wire card, and on one end of such roller I fix a ratchet wheel provided with a pawl. The velvet or other fabric to be finished, passes over this wire card roller, then back under a plain tension roller placed beneath the plate, and then forward to the ordinary card covered roller which draws the piece through the machine. The consequence of this arrangement is that as the wire card on the first-named roller takes a firm hold on the back of the velvet or other fabric and the ratchet wheel prevents the action of the ‘peg’ from drawing the velvet or other piled fabric backwards, and thus the finishing or ‘pegging’ of the said fabric may be commenced close to the front end thereof instead of about a yard from the end as ordinarily practised.”

The above is the provisional specification. The complete specification with one drawing, is published at 4d.

A.D. 1876, December 23rd.—No. 4970.

ASHCROFT, JAMES. “Improvements in the Construction of Bleaching Kiers.”

“This invention relates partly to kiers used for bleaching goods, such as require the headings to remain outside the kier during the bleaching operation, and partly to kiers used for bleaching other goods.

“In bleaching goods such as muslins with gold headings and other goods with coloured headings which will not bear bleaching, it has been usual to leave the cover off the kier and to allow the headings to hang over the edge.

“To obviate the necessity for leaving the kier open, I form two openings in the opposite sides of the kier at the top, and when placing the goods in the kier I pass the headings out through these openings. Over the headings are placed blocks of wood of suitable form, and above these a plate of iron furnished with a groove in the edge. This plate of iron is then screwed down by means of bolts until it is level with the top of the kier, forcing down the wood block and holding the headings firmly between it and the bottom of the opening.

The groove in the edge of the plate is now level with the sliding cover of the kier which may be then slipped into the groove and closed in the ordinary manner. The screw bolts are enclosed in grooved bars so as to prevent them from coming into contact with the goods. The sides and bottom of the openings are also made with grooves, so that when it is not required to leave the headings outside the kiers, sliding plates or shutters may be lowered into the groove so as to close the openings entirely.

"Another part of my invention consists of an arrangement applied to the safety valve to shut off the steam at any given pressure. At the bottom of the pipe leading to the safety valve I have a smaller valve calculated to lift at a lower pressure (say, at about half-a-pound less to the square inch). The spindle of this valve works through a perforated plate, and when the steam in the kier has reached a pressure of half-a-pound below that at which the safety valve would blow off, it lifts this small valve, and the steam thus liberated lifts a cup-shaped valve above it, the rod of which passes out, steam-tight, through the rod of the safety valve, and is attached at its upper end to one end of the lever. This lever is supported on a fulcrum at the centre, and its other end is connected by a slotted link to the key of a tap in the steam pipe which admits steam to the kier, the result of which arrangement is that as soon as the steam lifts the smaller valve, its rod causes the lever to close the steam tap partially, so as to reduce the amount admitted. This amount may be regulated by altering the length of the link, or by engaging the key of the tap in a different slot."

The above is the provisional specification only; the complete specification, with six figures on two sheets of drawings, is published at 6d. It may be noted that, between the application for and sealing of the patent, James Ashcroft died, his widow and administratrix, who completed the patent, says, "With regard to the second part of the invention, as described in the provisional specification, I wish to remark that my late husband made no communication to me, and I cannot find that he made any models or drawings of the same, and

therefore I do not wish to lay any claim to this part of the invention."

A.D. 1876, December 30th.—No. 5055.

GEDGE, WILLIAM EDWARD. "Improvements in the Manufacture of the Hydrocarburets of Coal Tar, and of the Amines derived therefrom." *A communication from Leon Hiernaux. (This invention received provisional protection only.)*

The provisional specification is a short treatise, from an original point of view, concerning aniline and its analogues; it is full of chemical symbols and formulae. The only point of practical information as to the idea of the inventor would appear to be in a paragraph where it is stated.

"In short, by this invention aniline may be manufactured directly and with great economy, by heating together in a closed vessel coal-tar and ammonia, but it requires practical conditions, proper proportions, and uniformity of mixture, temperature, pressure, and duration of the reaction."

A.D. 1877, January 8th.—No. 84.

BIRCH, WILLIAM. "Improved Self-acting Machinery for Opening, Smoothing, Spreading, and Guiding Fabrics for the use of Bleachers, Dyers, Calico Printers, and others."

"The objects of my invention are certain improvements of the apparatus composing the machine, for which Letters Patent, No. 2610, dated 1st October, 1870, were granted to me, by which improvements such machines become more easily adjustable for work, are much simplified, and their manufacture facilitated.

"The improvements consist in the substitution of revolving rollers or cylinders having right and left handed screw threads on their surface in the place of the endless chains or bands that draw out the fabric, passing through the machine laterally from the centre towards the selvages. The screw threads project considerably above the surface of the rollers, and are formed of some thin material that has some grip upon the cloth or fabric without being sharp and cutting; they run from the centre towards the ends to the right and left on

one roller or pair of rollers, and to the left and right on the second or second pair, gearing respectively with the former or former pair. These rollers can be applied in the same way as the chains or bands used hitherto, and as described and set forth in my specification before mentioned, in which case I modify the modes of driving in the ordinary way. I prefer, however, to employ one pair or two rollers going right across the machine, instead of two pairs as at present arranged. They are either placed side by side or one above the other, according to circumstances. The axis of the one that receives a revolving motion by means of wheels or pulleys is stationary. This one imparts motion to the other roller by means of spur wheels or bands from the centre. The second or driven roller is supported in such a manner that it may oscillate longitudinally round an axis perpendicular to its own axis, and the plane in which it may oscillate so as to get near to the other roller on one side and farther away from the other side, *i.e.*, form an angle with it. This is effected by means of an oblong swivel frame surrounding the swivel roller, and carrying at its ends the bearings in which the roller revolves, the frame itself being supported on two arms projecting from the centre of its longer sides. The swivel roller is connected to the regulator in a similar manner as the endless chains or bands before described, so that the material which is passing through the machine, when running from its central course to one side, acts upon the regulator, which in its turn brings the swivel roller nearer to the other on that side, from which the material has gone, thus increasing the hold of the screw threads upon the material on that side, while on the other side the opposite is taking place, the effect being similar to that described in the specification alluded to.

“Important points in my invention are the substitution of screw rollers for endless bands or chains, the arrangement of the gearing between the two rollers, the swivel support of one of them, and the combination of the swivel roller with the governor or regulator.”

The foregoing is the provisional specification only, the

complete specification, illustrated by six figures of the machinery upon one sheet of drawings, is published, price 6d.

A.D. 1877, January 12th.—No. 169.

TONGUE, JOHN GARRETT. "Improvements in Means and Processes for Obtaining Colouring Matters from Cannel, Anthracite, and other Coals, Applicable to Various Useful Purposes." *A communication from Doctor Meusel, of Breslau. (This invention received provisional protection only.)*

"According to this invention, fossil coal, or cannel coal, or anthracite or boghead coal, are treated advantageously in fine powder with oxidizing chemical compounds by ordinary or higher temperatures in suitable vessels.

"The most advantageous method of carrying out these improvements, is to heat the different coals finely powdered with nitric acid or with potassic or sodic nitrate and sulphuric acid. Also potassic chlorate or potassic chromate, or hypochloride of lime or compounds of manganese, may be used for the reaction with or without an acid.

"By the action of nitric acid or nitrates with acids, compounds of nitrogen with oxygen are developed, which are to be used in the manufacture of sulphuric acid or of salts containing nitrogen bound to oxygen.

"Coals treated in the above manner undergo a great change; a great part of the coal can now be extracted by caustic or alkalis, and by ammonia, or by the carbonates of soda or potassium or ammonia advantageously by heating the solution of alkalis with the product of the above treatment, a deep brown coloured solution and a black residue is so obtained.

"The black residue is a deep black covering colour, which may be used for lime colour (glue colour) or oil colour, or with bone black, or instead of bone black, soot or graphite. It may also be applied for the black for printing or for blacking and washing, painting, besprinkling, or other like purposes.

"The brown solution of the alkali salts may be used directly for colouring, for instance, by fluids, by soap, or otherwise.

"The solutions give by evaporating the alkali salts, and by

decomposition with metallic salts, new salts of metals which are to be used as colours.

"By the method of decomposition the salts of strontian, of barium, of magnesia, of aluminium, of maganese, of iron, of cobalt, of nickel, of zinc, of cadmium, of lead, of tin, of copper, and chromic oxyde are obtained. All these bodies are black or black-brown or brown colours, which may be mixed with other colouring matters. They can be used for painting, printing, and colouring. These colours are obtained as precipitates, and can be purified by water.

"The alkali solution can also be decomposed by the soluble metallic salts above (cotton or wool) and may so be used by the dyer.

"The alkali solution can also be decomposed by acids; a black-brown precipitate is obtained which may be washed in water, and which may also be used as a colouring matter. This black precipitate is the acid in which the coals are partly converted by the treatment with oxydizing compounds.

"By the above described means, fossil coal is oxydized, and the black residue obtained by the decomposition of the oxydized fossil coal may be applied as a colouring matter to various useful purposes.

"The product of the oxydation of fossil coal is soluble in alkalis, and the compounds of this product of oxydation may be applied as a colouring matter to various useful purposes."

A.D. 1877, January 20th.—No. 266.

CHADWICK, JAMES. "Improvements in Printing Textile Fabrics." (*A communication from James Harley, of Massachusetts.*)

"This improvement is in relation to the one for which Letters Patent were granted to me bearing date the 21st day of February, 1876, No. 717, being, like the present one, a communication from the said James Harley, of Lowell, United States of America, and consists in printing or applying fast greens, blues, violets, or purples, known by the name of iodine or methyl greens, blues, and violet colours on textile fabrics, either by themselves or in combination with or simul-

taneously with alizarine or madder extract colours, or any other colours which after printing have to be aged, steamed, and soaped, or washed off.

"The invention is carried out as follows:—I take for my green colour at the rate of about one gallon of sumac extract, one gallon of acetic acid, two gallons of water, eight pounds of crystal starch; boil, then add two pounds of tartaric acid; cool, then add twelve ounces of methyl green. The colour is then ready for printing on the cloth.

"To make my blue and purple I take at the rate of one gallon of sumac extract, one gallon acetic acid, two gallons water, eight pounds crystal starch; boil, then add two pounds of tartaric acid; cool, then add aniline purple or blue, according to shade required. The colour is then ready for printing on the cloth. I take cloth which has been bleached, and pass it on to the printing machine, when the colours are printed on. The printed cloth is then aged by hanging up two or three days, or passed through an ageing machine. The printed cloth is then steamed, and afterwards passed through the soaping or washing operations, and finished in the usual manner of printed fabrics.

"Having now described the nature and particulars of the said invention, I desire it to be understood that I do not confine myself to the exact proportions or materials hereinbefore described, as an expert chemist may substitute materials for many of them, but what I claim is,—

"First. The improved process of making iodine or methyl greens, violets, and blue colours fast by the means described.

"Secondly. Printing in fast iodine or methyl greens, violets, and blues, fixed as described, either alone or in combination with alizarine or madder extract colours, or any other colours which are aged and steamed after printing without being dyed."

3. *British and Foreign Patents, from the Commissioners of Patents Journal, July 24th to August 24th, 1877, inclusive.*

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Colouring Matters, Dyes, Pigments.

674. MICHEL EDMOND SAVIGNY, Chemist, and ALFRED CHARLES COLLINEAU, Doctor in Medicine, both of Boulevard St. Denis, 1, at Paris, for an invention of "The manufacture of an improved vegetable colouring substance and the derivatives thereof."—Dated 19th February, 1877.—This patent has passed the great seal.
2602. WILLIAM ROBERT LAKE, of the firm of Haseltine, Lake, and Co., Patent Agents, Southampton Buildings, London, for the invention of "An improved manufacture of red colour."—A communication to him from abroad by Johann Zeltner, of Nuremberg, Bavaria.—Provisional protection has been granted.
2614. WILLIAM ROBERT LAKE, of the firm of Haseltine, Lake, and Co., Patent Agents, Southampton Buildings, London, for the invention of "Improvements in the manufacture of violet colour."—A communication to him from abroad by Johann Zeltner, of Nuremberg, Bavaria.—Provisional protection has been granted.
2649. ADALBERT WACHHAUSEN, of Wiesbaden, Germany, Doctor of Philosophy, for the invention of "An improved brown colour or dye and process for obtaining the same."—Provisional protection has been granted.
2841. FELIX DE LALANDE, of Rue d'Enfer, 22, at Paris, Civil Engineer, for an invention of "Improvements in the treatment of alizarine for the production of different colours or hues therefrom in dyeing and printing."—Dated 18th August, 1874.—This patent has become void.
1425. JOHN CASTHELAZ, of 19 Rue Sainte Croix de la Bretonnerie, in the city of Paris, Merchant, for an invention of "Improvements in the manufacture of artificial alkaloids derived from coal tar, and in the preparation of salts of the said alkaloids."—Dated 18th May, 1870.—The £100 stamp duty has been paid.

- 186,485. L. LEIGH, of Pittsfield, Mass., for "Preparing aniline dyes."—Application filed 23rd October, 1876.—United States.
- 42,533. H. DEQUIN, for "A new dye for cloth, wool, &c."—Dated 28th June, 1877.—Belgian.

Bleaching.

2945. RICHARD PENDLEBURY, of Newton Heath, near Manchester, in the county of Lancaster, Bleacher, for an invention of "Improvements in apparatus used in bleaching."—Dated 1st August, 1877.—Provisional protection has been granted.
2991. ADOLPHE VIOL and CESAIRE PIERRE DUFLOT, of Paris, (France), Manufacturers, for an invention of "A new process of bleaching feathers."—Dated 6th August, 1877.—Provisional protection has been granted.
1900. ADOLPH ALEXANDRE PLANTROU, jeune, of Boulevard de Strasbourg, 23, Paris (France), Director of Manufacture, has given notice to proceed in respect of the invention of "An improved process of scouring and purifying vegetable and animal fibres and fabrics."
6. T. D. BROCHOCKI and Co., of Paris, for "A decolouring agent, called 'Concret d'eau de Javelle.'"—3 years.—Dated 6th January, 1877.—Grand Duchy of Baden.

Printing and Dyeing.

2513. WILLIAM MORGAN-BROWN, of the firm of Brandon and Morgan-Brown, Engineers and Patent Agents, of 38, Southampton Buildings, London, and 1, Rue Laffitte, Paris, has given notice to proceed in respect of the invention of "Improvements in printing textile fabrics."—A communication to him from abroad by Henry Dow Dupee, of Boston, county of Suffolk, State of Massachusetts, United States of America.
3123. EDWIN THURMAND, of Batley, in the county of York, for an invention of "An improved method of forming patterns or designs on felted fabrics."—Dated 16th August, 1877.—Application.
89. F. HEROLD, of Vienna, for "A machine for printing kerchiefs."—3 years.—Dated 5th June, 1877.—Grand Duchy of Baden.
- 186,620. JULIUS RAU, of Stuttgart, Germany, for "Processes for dyeing silks."—Application filed 4th August, 1876.—United States.

Squeezing and Drying Machines.

1005. WILLIAM SUMNER, of Manchester, in the county of Lancaster, Merchant, for an invention of "Improvements in apparatus for drying yarn, woven fabrics, and other materials."—A communication to him from abroad by Messieurs Tulpin Brothers, of Rouen, France, Machine Makers.—Dated 13th March, 1877.—This patent has passed the great seal.
1356. WILLIAM BIRCH, of Salford, in the county of Lancaster, Machinist, has given notice to proceed in respect of the invention of "Improvements in squeezing machines."
2766. JOHN STOTT, of the firm of John Stott and Brothers, of Wardle, near Rochdale, in the county of Lancaster, Woollen Manufacturers, and JOHN BARKER, of the firm of Jonathan Barker and Sons, of Todmorden, in the county of York, Engineers, for an invention of "An improved machine or apparatus for dyeing textile fabrics."—Dated 10th August, 1874.—The £50 stamp duty has been paid.

Yarn Treatments.

698. JOHN STIRLING ALSTON, Merchant, and WILLIAM REID, Dye Works Manager, both of Glasgow, in the county of Lanark, North Britain, for an invention of "Improvements in apparatus to be used in connection with various processes of treating yarns with liquids."—Dated 20th February, 1877.—This patent has passed the great seal.
2658. THOMAS DICKINS, ALBERT LANGLEY DICKINS, and HARVEY HEYWOOD, all of Middleton, in the county of Lancaster, Dyers and Printers, for an invention of "Improvements in machinery or apparatus used in dyeing yarns or threads of silk."—Dated 30th July, 1874.—This patent is void.
41. K. H. WEISBACH, of Chemnitz, for "A rotary machine for drying yarn."—3 years.—Dated 3rd March, 1877.—Grand Duchy of Baden.

Wool Treatments.

2208. ANDRE' PROSPER ROCHETTE, of Petit-Quevilly, près Rouen, in the republic of France, for the invention of "Improvements in washing wool, and in solutions employed for this purpose."—Provisional protection has been granted.
- 425,16. A. DICKTUS, for "A process for rendering vegetable sub-

stances in woollen fabrics invisible."—Dated 26th June, 1877.—Belgian.

Finishing Treatments.

859. JOHN WILSON, of the firm of John Wilson and Company, and WILLIAM COCHRANE, both of Glasgow, in the county of Lanark, North Britian, for an invention of "Improvements in hot pressing textile fabrics and in the machinery or apparatus employed therefor."—Dated 3rd March, 1877.—This patent has passed the great seal.
1066. SAMUEL MILNE SMITH, CHARLES TELFORD SMITH, and WILLIAM BINNS, of the firm of Samuel Smith and Company, of Bradford, in the county of York, Dyers and Finishers, have given notice to proceed in respect of the invention of "Improvements in finishing 'moreens' and corded fabrics."
1210. WILLIAM EDWARD NEWTON, of the Office for Patents, 66, Chancery Lane, in the county of Middlesex, Civil Engineer, has given notice to proceed in respect of the invention of "Improvements in machinery or apparatus for stretching fabrics." A communication to him from abroad by Alfred François Lacasaigne, of Paris, in the republic of France.
2724. BRISTOW HUNT, of Serle Street, Lincoln's Inn, in the county of Middlesex, Gentleman, for the invention of "Improvements in machinery for plaiting fabrics."—A communication to him from abroad by Hermann Albrecht, of Philadelphia, Pennsylvania, United States of America.—Provisional protection has been granted.
2748. JOHN SMITH, of Collyhurst, in the city of Manchester, Bleacher, Dyer, and Finisher, for an invention of "Improvements in beetling machines."—Dated 8th August, 1874.—This patent is void.
1. P. MAGNER, of London, for "A process of treating vegetable fibres to impart to them a silky appearance, and for preparing them for dyeing."—3 years.—Dated 2nd January, 1877.—Grand Duchy of Baden.
82. R. W. WALLACE, of London, for "Treatment of vegetable fibres for giving them a silky appearance and preparing them for dyeing."—1 year.—(Secret.)—Dated 6th March, 1877.—Austrian.

THE TEXTILE COLOURIST.

No. 22.]

OCTOBER, 1877.

[Vol. IV.

1. *Loss and Recovery of Indigo from Vats.*

AT various times attention has been directed to the recovery of indigo from the vat bottoms after the colouring matter had been abstracted as far as possible by the usual dyeing processes. Most dyers who have attempted to recover the indigo believed to exist in the vat bottoms have not found it worth while continuing the processes, the indigo actually recovered scarcely paying for the cost of material and labour. Some experiments have lately been made upon this subject which we find recorded in the *Muster Zeitung*, No. 33, 1877, and are worth recording. M. Feron doubted if there was any appreciable quantity of indigo left in the vat bottoms when the whole process had been conducted with proper care, and he made an experiment to ascertain whether he was right. He set a vat with 5 kilogrammes (11 lb.) of Bengal indigo, using copperas and lime in the usual way, and then dyed in it until it was exhausted; he then run the clear liquid into a cask and collected the bottoms in another and added hydrochloric acid to both until the liquids were acid. This was with the intention of dissolving out all the free lime and the oxide of iron, so as to set free any indigo that might be combined or held back by these substances; after the liquids had settled, the clear fluid portion was run away and the insoluble matters collected upon a linen filter and washed

several times with water. These insoluble matters weighed 6 kilogrammes, and must have contained whatever indigo there was left in the vat after the conclusion of the dyeing. To ascertain if there was any indigo in the substance it was dried, finely pulverized and treated with Nordhausen sulphuric acid, afterwards diluted with water, filtered, and the liquid examined in a colorimeter, but no trace of blue colour could be seen. Again the residue was treated with a large quantity of hydrochloric acid, and tested again to see if it would yield any sulphate of indigo, but none was obtained. Hence, M. Feron concluded that the residue contained no indigo, and that the dyer had no reason to fear loss of indigo in dye vats if the indigo is properly ground; or at any rate, that the amount of colouring matter lost was so insignificant that it was not worth while recovering.

These experiments were reported upon by M. B. Tantin, who repeated them with some variations. He observes that Berzelius stated that when an excess of lime was in contact with reduced indigo it formed an insoluble compound which could not therefore be useful in dyeing, and must lead to a loss of colouring matter. But the experience of scientific and practical men as Schlumberger and Schwartz do not confirm this statement of Berzelius, while others incline to admit it. Calvert reports that by simply treating vat bottoms with hydrochloric acid, a considerable quantity of indigo can be recovered, and quotes a case in which indigo to the value of 120 francs was recovered at a cost of 50 francs. Tantin repeats the account of Feron's trial, stating that the indigo used contained 62.5 per cent. of indigotine, that the greatest care was taken in setting the vat, and that it was exhausted by dyeing to the utmost extent. He re-examined the residue obtained by Feron, but in a different manner; instead of Nordhausen sulphuric acid he employed the powerful reducing agent hydrosulphite of soda, which shewed the presence of indigo, and by repeatedly treating the residue as long as it shewed any signs of indigo he eventually obtained 1.020 grammes of indigotine from 50 grammes of the residue, that is about 2 per cent. of its weight. To calculate what

percentage relation this bore to the original quantity of indigo employed, and using the French weights, it is found first that 5 kilogrammes of indigo at 62.5 per cent. are equal to 3.125 kilogrammes of indigotine, and that the residue weighing 6 kilogrammes would therefore contain 122.004 grammes of indigotine, that is, 3.92 per cent. of the indigo used, or nearly 4 per cent. Tantin considers that this loss is not considerable, and that the process of indigo dyeing leaves but little to desire, and concludes that the only point requiring attention is to have a very perfect grinding of the indigo; neglect of this may lead to very considerable loss.

If an actual loss of 4 per cent. of the indigo took place in an experiment which was conducted so as to prove, if possible, that no loss took place, with extraordinary care in the grinding of the indigo and preparation of the vat, and the vat exhausting by dyeing to the utmost, it may be suggested that it is very probable, under ordinary circumstances, with less careful working, and less exhaustive dyeing, that double and treble the amount may be lost.

Nothing is said in the report of the experiments as to what was dyed in the vat, whether cotton or wool, or whether, if cotton, plain cotton or printed with resists. If only plain cotton goods were dyed there was nothing to disturb the state of the vat, and it might be very completely exhausted, but the case is different in dyeing goods printed with resists, for these precipitate the indigo in a state in which it is not easily redissolved by the copperas and lime, and much more indigo would remain in the bottoms than with plain goods.

In Underwood's paper upon the subject of recovery of indigo* it is shewn that the vat bottoms from the navy blue style of dyeing do contain a considerable quantity of indigo; whether it will pay for extraction must depend upon a variety of circumstances, but that there is unexhausted indigo in all vat bottoms must be evident to the most superficial observation. M. Feron's attempt to extract the indigo left in the bottoms by means of sulphuric acid, thinking to make sulphate

* *Textile Colourist*, 1, p. 193.

of indigo of it, shews but little knowledge of the subject. Underwood states that orpiment and soda are the best materials to use in practice, but even this powerful mixture has to be repeatedly boiled with the bottoms to extract all the indigo, and he mentions as many as twelve or fourteen successive boilings. At the time this paper was written hydrosulphite of soda was not known ; it is doubtful whether it is more energetic than orpiment and soda, but M. Tantin had no difficulty in extracting indigo by its means from the residue declared to contain none, and correcting the too hasty conclusions of M. Feron.

There must be loss of colouring matter in nearly every kind of dyeing. It cannot be expected that the water will yield up the whole of the dye in solution to cloth, even in those cases where the water seems colourless, as in some cases of dyeing with aniline colours it is seen by looking at it in bulk that there is colour left which may amount to 4 per cent., more or less, of the dyestuff employed. There is no dyestuff, however, which can be recovered as indigo can be, or which will stand or repay so many treatments. The necessity of a thorough grinding of indigo is well understood by the English dyers. It is often ground night and day for three or six weeks. There is not much room for improvement on that score ; but it would be well that they should examine their vat bottoms to ascertain that they are not losing indigo from other causes and throwing it away.

2. *Materials for a History of Textile Colouring.—No. 7.*

Nitrate of Tin, or Dyers' Aquafortis.—The following article is extracted from the notes to Parkes' Chemical Catechism, fourth edition, 1810. It is interesting in an historical point of view as being evidently written from direct observation

and communications with practical men, and contains some curious statements upon the properties of nitric acid.

"This article (dyers' aquafortis) is used for dissolving tin to form a mordant for fixing some of the most valuable colours on woollen cloths. In employing this acid the dyers in the Metropolis generally proceed thus:—A carboy of aquafortis is measured out into a large earthen pan, with from 1 to 2 quarts of water for every gallon of the acid, and the whole is well mixed by stirring it with a strong wooden spatula.

Supposing simple aquafortis to be used, the quantity of water to be employed amounts to about one-third of the whole; but as no fixed rule can be given, this is left to the discretion of the workman, who apportions the quantity according to the nature and strength of the acid he is using. When the aquafortis and water are thus united, a few handful of grain tin are then thrown in such a manner as nearly to cover the whole of the bottom of the jar. An action immediately commences, and if the aquafortis be properly prepared and the tin uniformly spread, the solution goes on regularly, and no more heat is generated than is necessary to keep up a proper action.

If a froth appears upon the surface, the whole is well stirred with the spatula for a few seconds, as it is known that the froth is frequently occasioned by the tin lying in heaps at the bottom of the vessel. When the tin is dissolved more is thrown in, and stirred as before as occasion requires. If the aquafortis be pure, it will now be necessary to add a portion either of common salt or salammoniac to the mixture, which is given in such quantities, and such intervals, as the appearances of the acid may suggest. Here the discretion of the workman is the only guide; for in this as in many other cases, practice instructs better than precept.

When rather more than half the usual quantity of the tin is dissolved, the liquor begins to turn, as it is termed; that is, a portion of the yellow oxide collects round the mass of tin at the bottom of the vessel, which when stirred gives colour to the supernatant liquor. When the aquafortis is in a proper state, the colouring always commences at the bottom of the jar, which

increases on the further addition of the tin till the whole liquor acquires the colour of rum, or rather of bright amber. If the aquafortis be good these appearances always take place; if not, the tin may dissolve, but the liquor as it becomes saturated will acquire a milky, instead of a yellow appearance, which shews that the tin is improperly oxidized by the acid, and that such aquafortis is totally unfit for use.

It has been doubted whether a solution of tin could be made with pure nitric acid, and this much is certain, that the tin will remain only a short time in solution unless a portion of muriatic acid also be present. The mordant, therefore, that the dyers use for scarlets is a proper nitromuriate of tin. In order to produce this, that is, to convert the nitric to the nitromuriatic acid, it is that common salt or salammoniac is employed; for either of these salts becomes decomposed by the aquafortis, and the muriatic acid thus liberated performs its part in composing the solution.

Aquafortis is employed in a variety of trades, such as brass founders, silver refiners, gilders, leather dyers, and calico printers; but such aquafortis would be very improper for dyeing woollen cloths. Nothing can be better known to the dyers in the large way, than that the majority of the aquafortis that is manufactured is entirely unfit for dyeing scarlet. Few there are of this occupation who have not occasionally met with an article of this kind; and whenever this happens they know of no remedy but that of exposing it to the atmosphere to absorb oxygen, or laying it by for nine or twelve months to acquire age as they term it.

Formerly, the difficulty of making good dyers' aquafortis was so great that the whole which was consumed in these Kingdoms was actually imported from Holland, and there are people now living who remember the time when they never thought of using any but Dutch aquafortis. Owing, however, to various causes, the English dyers are now generally supplied from London, or by some particular manufacturers in the country who have paid a particular attention to the production of this distinct article. But even now there is so much uncertainty in it that many large dyers

never use any aquafortis till it has lain in their warehouses for twelve months, that the component particles of the acid may unite more intimately and thereby form that mild form of aquafortis which readily dissolves tin without rendering any part of it an insoluble oxide.

Often reflecting on the inconveniences thus resulting to the dyers; also, on the loss of interest upon a large capital thus lying dormant; and on the disappointment often arising from the use of a proper article, I instituted a series of experiments on nitrous acid in the hope of removing these difficulties; and it is only since the publication of the second edition of the Chemical Catechism that I was enabled to discover that if aquafortis be distilled in a peculiar way it is as fit for the use of the dyer in twelve days as it is after being kept twelve months. The knowledge of this fact is the reward of some thousand experiments, attended with considerable expense and of several years patient investigation.

To those persons who are not sufficiently acquainted with the process of forming the solution of tin, a few directions may perhaps be acceptable.

(1) To prepare the tin, melt it in an iron ladle, and continue it on the fire till it be considerably hotter than its melting point. When in this state let one man pour it from a height of several feet into a tub of cold water, while another constantly agitates the water with a few wooden rods.

(2) In making the mixture of aquafortis and water, use as little water as possible, consistent with the nature of the aquafortis employed.

(3) In adding the first portion of tin, put in such a quantity as by its action shall soon raise the temperature of the liquor to about 100° F. To effect this a larger quantity must be added in winter than in summer. If the aquafortis be good it is best to stir the mixture incessantly for about five minutes on the first addition of the tin, which hastens and improves the process. Much, however, of the aquafortis that is sold would fire, as it is termed, by this treatment; that is, the violence of the action would decompose the acid, a great part of which would evaporate and be entirely lost in dense red fumes.

(4) When the mass has acquired the heat before mentioned, the tin should be added in such portions only as will preserve it at about the same temperature.

(5) Add no salt to the solution till there is an appearance of white oxide collecting at the bottom of the jar. If salt be then added and stirred with the mixture, this oxide will be taken up with the fluid.

(6) If the solution of tin be designed for dyeing a perfect flame-coloured scarlet, be careful to add no more salt than is absolutely necessary to keep the tin in solution. If a rose-coloured scarlet be desired it will be desirable to add a further portion of salt, according to the colour intended to be produced.

(7) When the solution has acquired the proper colour no more tin should be added, as a saturated solution of tin does not produce such bright colours as one that is in a lower state of saturation. The quantity of tin employed is generally about an eighth of the weight of the aquafortis in which it is dissolved.

It will be of some interest to compare this account, dating probably from about 1800, with another practical account of the preparation of the same mordant three-quarters of a century later. This is to be found in the *Chemical Review* for November, 1875, and bears all the marks of coming from some one intimately acquainted, both scientifically and practically, with the matter. The following is from the notes on mordants in that publication:—"In a great many establishments where cochineal colours form a prominent department we shall see an experienced workman pour into a broad and perfectly clean stoneware bowl a certain known quantity of a liquid which he designates 'single aquafortis,' and which is otherwise known as 'dyers' aquafortis,' it being required by no other consumers of nitric acid. If we examine this liquid we shall find that it marks about 32° or 33° Tw. It is colourless, and, if tested, will be found perfectly free from sulphuric acid, and, as far as possible, from the lower oxides of nitrogen. But if diluted with distilled water, and mixed with a few drops of solution of nitrate of silver, a white curd-like

precipitate appears, shewing the presence of a certain quantity of muriatic acid. Having put the acid in the bowl he weighs out fine grain bar tin, not feathered, in proportion of 1 lb. metal to every 8 lb. acid. He then lays a few of the rods on the bowl and allows them to dissolve. In the number of rods thus taken to start the process, he is guided by the weather. The warmer the day the smaller amount of tin is put in at the commencement. If it be very hot, even a single rod may prove too much, and under such circumstances it is needful to begin with a small handful of dry feathered tin, adding the rods by degrees when action is once set up. If the operation is correctly managed the rods seem to melt quietly away without effervescence, and after a short time the liquid, which was at first as colourless as water, turns to a rich deep amber colour. All that is then required is to add the remainder of the tin gradually, neither allowing the action to die out for want of material, nor to become too rampant from over feeding. On no account must bubbles of red gas be allowed to form.

If the acid is not of good quality, or if too much or too little tin has been added in the first place, the process takes a different course. The amber colour does not appear, and the liquid, according to circumstances, may remain for some hours without changing colour, and then become turbid; or if too much has been added it may set up a violent action, giving off copious red fumes, and depositing a precipitate. In all these cases the spirit is spoiled. The addition of about half a pint of nitrate of tin of a former make to the aquafortis at starting is a very good plan to insure success. The finished nitrate of tin is a clear liquid of a deep amber colour. It stands at about 60° Tw. or upwards, and contains about 2¼ oz. of tin to the pound. In cold weather it will remain clear and fit for use for three or four weeks; but if the thermometer rises to 80° F. it will scarcely keep for a day without becoming turbid. This compound, which is probably a mixture of the nitrate of sesquioxide of tin, is generally used by the Yorkshire dyers under the name of nitrate of tin, scarlet spirits, or bowl spirits. It is used for cochineal colours upon woollens

or worsteds, and also as a mordant for the cotton warps of mixed stuffs, especially for certain fine clarets and browns. Having ourselves frequently seen it made and used, we naturally feel some surprise at hearing it spoken of as something fabulous. . . . But the name 'nitrate of tin' is also unfortunately given by some authors and some practical dyers to a totally different preparation, or set of preparations; we mean to one or more of the spirits made from mixtures of ordinary double aquafortis (nitric acid at about 66° Tw.) with spirits of salts, the latter being largely in excess. Such spirits are colourless, or have at most a faint yellow tinge derived from chloride of iron present, and are merely perchloride of tin, mixed in some cases with a little protochloride. Such compounds may be fairly named nitro-muriates, but to call them nitrate is decidedly an error."

Because strong nitric acid when it acts upon tin behaves differently with it than with most other metals, and instead of forming a nitrate forms an oxide insoluble in nitric acid, it is pretty generally concluded that there is no nitrate of tin properly so called; or at any rate, that if there be a nitrate of tin it cannot be produced by directly acting upon tin with nitric acid. There is no doubt of the existence of nitrates of both the stannous and stannic oxides. Proust long ago shewed that diluted nitric acid acted upon tin at the ordinary temperature without evolving nitrous acid, but with formation of ammonia. Berzelius obtained a stannous nitrate by dissolving the oxide in dilute nitric acid, and the stannic nitrate in the same manner (Gmelin, v., p. 92). Both compounds are very unstable, being decomposed by a slight elevation of temperature. From the fact of the writer in the *Chemical Review* stating that the dyers' aquafortis contained some muriatic acid, it might be objected that this explained the solution of the tin; but tin dissolves in pure nitric acid. Some experiments were made upon the solution of tin by nitric acid in the editor's laboratory; the acid was pure, sp. gr. 1.170 or 34° Tw., the temperature kept at 60° F. There was always evolution of gas, and this gas being collected and

analyzed, it was found that one gramme tin yielded in three experiments 58 c.c., 44 c.c., and 50 c.c. gas, and that 95 per cent. of this gas was nitrous oxide or laughing gas, the remainder appeared to be nitrogen. There was always formation of ammonia in the solution of the tin, one quantitative experiment shewed that the solution of 1 gramme tin produced 0.027 gramme of ammonia. Both stannous and stannic oxide were always found to be present in solution; in one case where one gramme of tin had been dissolved, the solution was immediately tested to determine the quantity of each oxide present, and it was found that 0.303 of the tin was present as stannous oxide, and 0.697 as stannic oxide, that is supposing there was no other oxide of tin; if there is a sesqui-oxide of tin in the saline state these figures would tend to shew that it probably exists in this solution. The results, however, vary so much by a slight change of temperature, and the conditions necessary to obtain them uniform so difficult to seize, that the examination was not completed.

3. Upon Silk Printing.*

Styles derived from Archil.—Archil is frequently used for the production of violet colours, although we prefer the less fugitive colour obtained from logwood.

The archil is used either in the form of an extract or as an archil lake. We shall call the lakes by the name of Parme to distinguish them.

Violet No. 1.

Archil at 22° Tw.	1 gallon.
Thick gum water	½ „
Alum	2½ oz.

* Abridged from Koepelin, "Impression des Etoffes de Soie." Continued and concluded from p. 65, vol. iv.

No. 2 violet may be made by taking 8 measures of gum water to 1 measure of No. 1 violet.

The parme lake is prepared by dissolving the colouring matter of the archil in a solution of carbonate of soda (25 per cent. of the archil) and adding to it a solution of alum. The alumina precipitates in a gelatinous state and takes down with it all the colouring matter of the archil, the liquid which floats above being nothing but sulphate of soda is decanted, and the precipitate collected and drained upon a filter.

Parme No. 1, for Outline.

Parme lake	2 parts.
Gum water	1 „

Weaker colours are made by reducing with gum water.

The printed goods are fixed in the ordinary way and washed. The colour at this stage is reddish, it is turned violet by passing it into water rendered alkaline by milk of lime and ammonia. The goods are worked for some minutes in the alkaline fluid, and then washed in running water. If caustic or calcined magnesia be added to the colour before printing this operation is unnecessary, the colours being developed without it; but the slightest acid vapour which may come into contact with them, either during or after steaming, renders a subsequent alkaline treatment necessary. As a remedy against the turning of the colours in steaming, the goods may be wrapped in greys which have been passed into water made milky by ground chalk, and then dried up without washing. The chalk remaining in the grey is calculated to neutralize the acid vapours which may arise in the steaming.

The improved archil preparation of M. Guinon (French purple) is so much more stable than the ordinary preparation, that all these kind of difficulties have been overcome.

With regard to coloured lakes, it may be remarked that any of them may be printed upon silk stuffs and give satisfactory results when it is desired to obtain soft or subdued effects. Since silk cannot be safely moistened so much as woollen before the fixing, it follows that the colouring matters

which exist in the state of precipitation cannot combine so intimately with the fibre; the shades produced are therefore not so deep or so bright as those obtained with the ordinary colours. If the steam is made too moist the colours run upon the stuffs and they become completely spoiled.

Application of Aniline Colours.—At the date when M. Koeppelin's work was published the aniline colours were in their infancy; but in a supplement printed some years later he gives the composition of a few aniline colours as applied to silk.

Aniline Pink No. 1.

Fuchsine in powder	1 oz.
Pure acetic acid	1½ pints.
Boiling water	1½ „
Gum water at 10 lb. per gallon	6 „

Reducing Mixture for Aniline Pink No. 1.

Thick gum water	7 pints.
Water	2 „
Acetic acid	¼ „

Aniline Pink No. 2.

Fuchsine in powder	1 oz.
Alcohol, pure	1½ pint.
Boiling water	1½ „
Gum water	6 „
Solution of carbonate of soda at 2 lb. per gallon	1½ „

Reducing Mixture for No. 2 Pink.

Gum water	4 pints.
Water	2 „
Alkaline solution above.....	¼ „

When acetic acid is used as the solvent for the fuchsine it should be very pure, for if it contains merely traces of essential oil the colour loses brightness and becomes bluish in the fixing. Pure alcohol alone or mixed with acid does not give the best results unless the acid is very pure. The No. 2 colour above has always given the best results. The fuchsine is dissolved in the alcohol, to which the boiling water is

added to assist the solution, the liquid is filtered and mixed with the gum water. The alkaline solution is then added, which preserves the colour and prevents it becoming dull if it has to be kept some time before it is all used up.

Aniline Blues and Blue Violets.—These colours which are obtained from the more or less complete decomposition of fuchsine by various reducing agents, are sold either as powders or in small lumps of a resinous appearance of a violet colour; they are soluble in alcohol or wood-naphtha, insoluble in cold water, and very little soluble in boiling water. The alcoholic solution added to water strongly colours it without precipitation; silks may be dyed in such a solution with success and of very fine shades. The dyed colours resist the action of strong acids, but are sensitive to light, which soon causes them to fade.

These colours are, however, preferable to similar shades obtained from archil or Prussian blue, both on the score of brilliancy and stability.

Purple No. 1.

Aniline blue violet.....	1 oz.
Alcohol	25 oz.
Water	12½ oz.
Gum water	50 oz.

Blue No. 1.

Aniline blue	1 oz.
Alcohol	25 oz.
Water	12½ oz.
Gum Water	2½ pints.
Sulphuric acid, 1 of acid to 16 water	2½ oz.

Reducing Mixture for both Colours.

Thick gum water	8 pints.
Water	4 pints.
Sulphuric acid, 1 of acid to 16 water	3½ oz.

For printing, the colours are dissolved in the alcohol which, is kept hot in a double-cased steam pan, the aniline is added by small portions, and well stirred and crushed until all has been dissolved, then the water is added boiling, the liquor filtered through sieving silk and the gum water added.

When redder shades of purple are required, the above purple can be mixed with the old aniline mauve, with which it associates very well and yields shades of great purity. The purple above, when considerably reduced, gives fine shades of grey of a special tint, which cannot be obtained from any other colouring matters. The same purple in mixture with archil, extract of indigo, and other extracts, gives all the fancy shades which can be desired. The blue colour should not be prepared long before it is to be used, for by keeping it has a tendency to become grey, losing its brightness. Such colour can be somewhat improved by adding a little more acid, or can be used up by mixing with fresh colour.

4. *Note upon the Collection of Designs at Peel Park, Salford.*

SEVERAL years ago the Editor, through the kindness of the obliging Curator of the Peel Park Museum, Mr. J. Plant, had an opportunity of leisurely inspecting the large collection of designs of printed calico which is possessed by that institution. This collection as is well known, was made for the express purpose of illustrating the progress of design from the year 1767, by a selection made from the pattern books of various houses. It was not, however, in relation to that department of calico printing that the following notes were made, but rather with a view of putting down the dates at which certain styles occurred in the collection. There was no opportunity of testing chemically whether the conjectures made with regard to particular colours was correct or not, and it is possible that in some cases good imitations may have misled the observer. The oldest specimen of calico printing in the museum is in a separate case, to which access was not obtained upon this visit, it was only seen through glass, it is a madder red, single colour, evidently printed from flat plate, and bears the date of 1751, Old Ford Works, London; the design is described as

being 6 feet 10 inches long, by 3 feet 2 inches wide, upon linen cloth; the subject is pastoral, and the impression produces all the details of an excellent engraving in the best possible way, the colour is remarkably good for a print of such early date. The large roll of specimens commences with the year 1767, but for this year and 1768 the designs are on paper only, mounted upon cloth, after that date they are on various fabrics.

1769.—Prevalence of indigo styles. Chintz and small furnitures in madder colours, the reds and pinks good, but the purples poor.

1770.—Covers or grounds of indigo blue, which are very similar to those produced by the precipitated or fast blue. Madder purples are of a bad reddish shade.

1788.—Covers over designs became general. There are dark ground prints of doubtful origin; seem fast colours as if an indigo bottom with dyed colour on top.

1793.—Continued prevalence of light indigo blue covers over madder work; the impression is strong that this blue is from the precipitated blue, although there is no authority for shewing that it was known at this date, it can only be this or the orpiment blue, which latter seems unlikely. Some of the madder purples are good.

1801.—Some good topical indigo blue printing, evidently the pencil blue or orpiment colour.

1810.—Fairly good samples of the neutral or lapis style, with blue, red, black, green and yellow colours; also what appear to be Turkey reds, with blue, yellow and green discharge upon or printed upon discharge white. Other blues in combination with various colours are evidently indigo blue pencilled in.

1814.—There is a large handkerchief shawl, with capital madder reds and pinks. Indigo blue and green in several styles.

1817.—A specimen which seems to be indigo blue, with chrome orange and yellow; and others which have the appearance of Prussian blue, with white, yellow and green discharge upon Turkey red. Pad purples of fair quality commence this year.

1818.—First observed iron buffs.

1821.—A good many China blues, and some blues suspected to be Prussian blue.

1824.—First rainbowing effects observed.

1827.—Chrome oranges and yellow common. Heavy purple pad prints first occur.

1829 and 1830.—First observed machine printed steam colours. Good dark blues and chocolates. Resist red under madder purples first seen. Steam greens and blues, numerous examples.

1836.—Plate madder pinks appear common, previous to this date, very few observed.

1847.—Samples of dyed work with catechu brown appear, none were observed previous to this date.

1850.—A notable change of styles observed ; glaring steam combinations disappear and much improved styles in madder and garancine are found.

The collection does not extend to any later date ; these notes do not pretend to fix the date of the introduction of any of the styles noted, but simply of their existence in this collection.

5. *Indigo Testing by Hydrosulphite of Soda.*

AMONG the processes of testing the value of indigo given in a recent supplement to this Journal no mention was made of the method devised by M. A. Muller in June, 1873, an account of which may be found in the Bulletin of the Industrial Society of Mulhouse, vol. xlv., p. 32. It seems a difficult and almost impracticable process to be accurately carried out by any but chemists accustomed to accurate manipulation and provided with all the resources of a good laboratory. It received some praise at the time of its introduction, and we think it well to give a translation of the paper and the report made upon it. They are in substance as follows :—

“ Before describing the apparatus used for the testing, I will give the method of preparing the hydrosulphite.

In a wide-mouthed bottle holding about 150 c.c., there is placed cuttings of sheet zinc rolled upon themselves as many as can be put in ; the bottle is then filled up with a concentrated solution of bisulphite of soda. In three-quarters of an hour the action is complete ; the liquid contents of the bottle are then poured into a phial and shaken up with 50 or 60 grammes of freshly slaked lime, the whole is diluted to the volume of 5 or 6 litres and filtered. This forms the test liquor.

As hydrosulphite of soda absorbs oxygen from the air with rapidity, it is necessary to conduct the testing in an inert atmosphere (carbonic acid or hydrogen). To accomplish this a Mohr's burette with a long tube is used ; in the tube a cork is fixed fitting into the central tubulure of a three-necked bottle which holds about 200 c.c. ; the other two necks are fitted up with tubes ; one, going to the bottom of the bottle, is for conducting the gas used ; the other tube opening from the top leads into a vessel of water, so that the gas passing through may bubble up through it. The inert or non-oxidizing gas employed is supplied by an apparatus in continual action, so that the current can be regulated at will. The stock bottle of hydrosulphite contains about 2 litres. It should be well closed with an india-rubber cork with two holes, one of which holds a tube terminating just inside the stopper, communicating with a supply of inert gas, which in this case may be ordinary illuminating gas ; the other holds a tube extending to the bottom of the bottle and connected with an india-rubber tube. When not in use these tubes are closed. To fill the burette its beak is connected with the india rubber tube, and the liquid sucked in by another tube fixed by help of a cork in the upper part of the burette.

Testing the Hydrosulphite.—An ammoniacal solution of sulphate of copper is decolourized by the hydrosulphite ; it forms the suboxide of copper which is held in solution by the ammonia. Under the same conditions indigotine blue is transformed into indigo white. Now I have found that to decolourize a molecule of sulphate of copper it requires

exactly the same volume of hydrosulphite as to decolourize a molecule of pure indigotine. These reactions are well defined and prove that the process employed is exact."

Omitting the formula we proceed :—

"By calculating the molecular weight of these substances, we find that 1 gramme of pure indigotine is decolourized by the same volume of hydrosulphite as 1.904 grammes of pure crystallized sulphate of copper. To prepare a standard solution, we therefore take 1.904 grammes pure crystallized sulphate of copper which is dissolved in water, and after adding an excess of ammonia the volume is made up to 1 litre. For testing the hydrosulphite, 50 c.c. of this liquid is taken and placed in the three-necked flask, and after passing gas through it rapidly for about thirty seconds the current is slackened and the hydrosulphite is run in until complete decolouration takes place.

Testing of the Indigotine.—Fifty c.c. of a sulphuric solution of indigo containing 1 gramme of indigo per litre are taken and boiled in a small flask to expel the contained air, and then introduced into the three-necked bottle, gas is passed through rapidly for thirty seconds, then more slowly, and the hydrosulphite run in until the colour becomes greenish-yellow, or a yellow more or less clear, according to the quality of indigo employed. In the case of low class indigo, the solution must be diluted with its own bulk of water, in order that the conclusion of the reaction may be clearly discerned.

Supposing that in a given case we have employed 14.3 c.c. to completely decolourize the 50 c.c. of solution of indigotine, knowing that to decolourize the same volume of the copper solution it requires 20.6 c.c.; the amount of indigotine in the sample can be obtained by the proportion—

$$20.6 : 100 :: 14.3 : x = 69.4$$

The following indigoes were tested by this process :—

	Indigotine per cent.
Bengal	69.4
Guatemala	60.3
Kurpah	51.6
Indigotine	100.0

Dr. Gopplesroder was requested to make a report upon the preceeding paper of M. Müller. He repeated the process in conjunction with M. Leonard and M. Trechsel, and he states as follows:—We followed scrupulously all the directions given by the author, both for the preparation of the hydrosulphite and the method of estimating its strength by means of the ammonical sulphate of copper and indigotine; the prepared indigotine by Fritsch's method with alcohol and glucose. We were careful to draw off only half the solution of indigo after it had been at rest for twenty-four hours. The indigotine obtained was washed with boiling water, then with a mixture of alcohol and water, and lastly, with boiling alcohol alone. The product was dried at 100° C., and we employed it to prepare the solution of sulphindigotic acid, representing 1 gramme of indigotine per litre. In testing this solution with the hydrosulphite of sodium we obtained figures agreeing very well; but it was not the same with the solution of ammonical sulphate of copper which M. Müller recommended for fixing the value of the hydrosulphite, we could not get constant results from it; this is owing to the termination of the reaction not being so sharply defined as with the indigotine. As an illustration, I give the figures obtained by M. Leonard: 20 c.c. of the standard solution of sulphate of copper required 13.5,—13.3,—13.7,—13.8 c.c., a mean of 13.6 c.c. of the solution of hydrosulphite of soda, while 20 c.c. of the solution of indigotine required 13.5 c.c. of the same solution of hydrosulphite in a series of six trials. The extreme difference is 0.5 c.c., which amounts to nearly 4 per cent.

In a series of trials by M. Trechsel the differences were still greater, being 2.3 c.c., or 15 per cent., is seen by the following amounts of the hydrosulphite required for 20 c.c. of the copper solution, 15—15.5—15.9—14.3—14.6—16.6—14.4—15.9; the mean being 15.2. In presence of this difficulty we endeavoured to replace the ammoniacal sulphate of copper by permanganate of potash, and obtained very good results. The solution contained 1.576 grammes permanganate per

litre, and in nine experiments made by M. Leonard and M. Trechsel the quantity of hydrosulphite required by 20 c.c. were respectively 9'2—9'2—9'1—9'1—9'2—9'1—9'1—9'1 and 9 c.c.; 20 c.c. of the indigotine solution required in four trials 6'0—6'1—6'1—6'2. From the greater concordance of these results, we believe that the permanganate will advantageously replace the ammoniacal solution of sulphate of copper.

M. Trechsel and myself are studying the relations which exist between permanganate, indigotine, and the solution of substance or substances called hydrosulphite. We shall determine exactly the equivalence between indigotine and permanganate of potash.

For the present we must be satisfied by summing up the result of the experiments as shewing that M. Muller's method of testing indigotine is the clearest and most accurate of all those we have had occasion to try, and which are described in special treatises. We must, however, state that the method of determining the strength of the hydrosulphite solution is not satisfactory; we suggest the use of permanganate, but probably better than that may be found. In the meanwhile we should advise the testing of samples of commercial indigo by the hydrosulphite, by comparing them with a standard or with a solution of pure indigotine. It remains to be seen whether the foreign matters which accompany indigotine in indigo do not act in some way to confuse the results. We cannot, of course, give an opinion upon this subject; it is only by comparing the results obtained by an analysis with those observed in practice on the large scale, in actual dyeing and printing, that we shall be enabled to know what degree of approximation can be attained by the use of the hydrosulphite; that is to say, that the direct method employed in practice, and which is founded upon the results obtained by actual dyeing will always be the practical test.

This process, it will be seen, is only a method of ascertaining how much hydrosulphite is required to decolourize by deoxidation a solution of sulphindigotic acid; the older pro-

cesses of testing the same solution act by destroying the colour by oxidation; the hydrosulphite method appears to have all the weaknesses of the old processes and some others special to itself arising from the remarkable instability of the testing liquid. We are not aware that M. Goppelsroeder has published any results of his experiments to shew the equivalence between indigotine and manganese in permanganate; if he is content to obtain his indigotine by Fritsche's process these results will be of no value, because that process cannot yield pure indigotine as far as our own experience goes. If sublimed crystallized indigotine be used, and that alone is reliable, we believe it will be found that there is no correspondence between manganese and chromium and the present admitted formula of indigotine. The amount of oxygen in chromates and permanganates required to destroy the colour of sulphindigotic acid should, according to theory, be one molecule for a molecule of indigotine, but actually a less quantity suffices, which suggests that either we have not got the correct formula for indigotine, or we do not know the compounds which it forms when decomposed by oxidizing agents.

6. *M. Michel de Vinant on Dyeing, Printing, and Bleaching.**

Another Black Mordant.—Acetate of iron at 5° Tw., thickened with British gum at the rate of 3½ lb. per gallon, dissolved by heating, cool and add about ⅓ part of nitrate of iron, at 110° Tw.

Chocolate Mordants.—These are mixtures of acetate of alumina and acetate of iron, in various proportions, according to the shade required; some illustrations may be given.

Chocolate for Blotch.—Equal measures of the acetate of alumina, No. 2,—which follows—at 8° Tw., and iron liquor at 7° Tw., thickened with British gum.

* Continued from vol. iii., p. 287.

Light Chocolate.—One measure of the black mordant above, at 8° Tw., and 2 measures of acetate of alumina No. 2, with addition of about 1½ oz. salammoniac per gallon of colour.

Acetate of Alumina, No. 2.—Twenty gallons of boiling water, 50 lb. alum, dissolve and add 5 lb. carbonate of soda, then add 38 lb. acetate of lead and ½ gallon of pure acetic acid at 10° Tw., leave three days to settle and use the clear, which should stand at 14° Tw. The dunging or cleansing is directed to be done either with silicate of soda alone, or in mixture with cow dung and bran, and in some cases chalk.

The dyeing, as directed by our author, is somewhat peculiar; first, for say two hundred handkerchiefs, 15 lb. of bran are boiled in a small quantity of water, and the decoction added to the water which is to be used for the dyeing; the dyeing material is a mixture of garancine and sumac, say 12½ lb. garancine and 6 lb. sumac, ox blood about 1½ gallon is added and the whole well stirred; then is added a solution of ½ lb. soap in a quantity of boiling water; after well stirring again the dye liquor is ready; the pieces are entered and worked at a very gentle heat, for fifteen or twenty minutes, and when it is seen the colour is taking evenly, the temperature is increased so as to arrive at the boil in about an hour; the pieces are then washed. The clearing is effected in boiling bran water and if the whites require it, the pieces are lightly soaped in cool soap solution, and afterwards passed in cold solution of chloride of lime. A peculiarity of this dyeing is that after the chloride of lime process, the goods are passed in weak muriatic acid and washed off.

Dyeing of Crimson on Printed Silk.—For one hundred handkerchiefs, boil 12 lb. of bran in some water, and add it to the dyebeck, wince the silk in the bran water cold two or three times, lift, and add 2¼ lb. cochineal in powder which has been previously boiled for twenty minutes with a little water and 6 oz. cream of tartar, then add 1 oz. powdered gall nuts and ½ lb. garancine. Let the pieces run fifteen or twenty minutes in the cold and when the colour is seen to be even, heat up to boiling in forty-five minutes, and

keep at the boil for four or five minutes. Clear with bran and water, but nothing else.

Upon the Printing of Wool and Muslin-de-Laine.—To put the pieces into proper condition after printing, the simplest method is to hang them in a room through which a current of warm air passes. A layer of sand, from 7 to 8 inches deep, is on the floor, which is kept moistened by degging, so as to have a constant degree of humidity in the air.

The pieces should hang in such a place twenty-four hours before steaming; they thus acquire a degree of moistness which is necessary for them in the steaming. The styles for madder dyeing are afterwards hung up in another room to dry for twenty-four hours.

Steaming.—The steaming box has a double bottom, the false bottom being full of small holes. On the real bottom a considerable depth of water is always kept, in order to secure moistness in the steam.

Lastings are steamed twice, one hour each time.

Druggets are steamed the same.

Merinos are steamed once for an hour and a quarter.

Light woollens and delaines are steamed once for an hour.

The lake colours are steamed as moist as possible for fifty or sixty minutes.

We extract some of the receipts given for colours upon woollens and delaines. The preparation, which is said to be the best adapted for printing, is made as follows:—

7 lb. oxymuriate of tin.

30 lb. commercial caustic soda, at 35° Tw.

Mix together. Separately dissolve

11 lb. oxalic acid in

1 gallon boiling water.

Mix the two solutions together, add water to reduce the strength to 2° Tw. when cold. Let the goods steep twelve hours in the liquor, or pad them without pressure at a strength of 8° Tw.; leave on the rolls twelve hours; wash and dry.

Dark Chocolate. Block.

8 lb. redwood extract, at 14° Tw.
 3 lb. logwood liquor, at 14° Tw.
 1 lb. bark liquor, at 30° Tw.
 3 lb. archil, at 18° Tw., mixed with
 3 lb. warm water; thicken with
 3½ lb. pipeclay.
 6¼ lb. dextrine, and add
 1¾ lb. alum,
 ½ lb. salammoniac, and when cold
 10 oz. crystals of nitrate of copper,
 3 oz. spirits of turpentine.

Chocolate No. 3.—Wool: 1¼ gallons peachwood liquor at 7° Tw.—5 pints logwood liquor at 7° Tw.—5½ lb. gum—10 oz. alum—5 oz. salammoniac. Dissolve, and when cold add—½ lb. nitrate of copper—2 oz. turpentine.

Chocolate for Roller No. 4.—Wool or silk: 2½ gallons strong archil—2½ quarts nitrate of alumina—1 lb. common extract of indigo. When the effervescence has ceased, add 9 lb. gum and dissolve at a gentle heat. Separately prepare the following mixture:—3¼ lb. starch—1 lb. gum substitute—1¼ gallons peachwood liquor at 14° Tw.—5 pints berry liquor at 7° Tw.—1 quart logwood at 14° Tw.—3 quarts acetate of alumina at 14° Tw., boil. Mix the two colours and heat them together under boiling point for fifteen minutes, put into a vessel and add 6½ oz. salammoniac and 6½ oz. alum, when dissolved add 1½ lb. turpentine and ½ lb. olive oil, and lastly, when quite cold, 1 lb. nitrate of copper.

Red No. 1, for Combinations.—1½ gallon cochineal liquor at 7° Tw.—1 pint sapanwood at 14° Tw.—½ pint berry liquor at 14° Tw.—3¼ lb. starch—¼ lb. oxalic acid—¼ lb. binoxalate of potash—4 oz. turpentine—4 oz. oil; boil, and when cold add 8 oz. bichloride of tin at 120° and 8 oz. oxymuriate of tin.

A solution of turmeric in alcohol or in acetic acid, can be advantageously used as a yellow part in reds, taking 3 lb. of either acetic acid or alcohol for 1 lb. of turmeric, and leaving them together for two or three days, then straining.

Red No. 2, for Wool or Delaine.—1 gallon water—1 quart acetic acid at 8° Tw.—4 oz. binoxalate of potash—3 oz. of tin crystals—2¼ lb. of cochineal. Boil the cochineal with the water and salts for one and a quarter hour and strain, boil the cochineal again with water, mix the liquors and boil down to 7 pints, then thicken with 2¼ lb. starch, add 2 lb. decoction of madder and 2 oz. olive oil, in which dissolve 1½ oz. white wax.

The above are specimens of the receipts given by De Vinant, in which the quantities are put into the best English equivalents possible. It is quite unnecessary to continue giving further examples of these colours, for the experienced colour mixer will see at once that they are very complicated, laborious, and by no means very practical; they seem to belong to a rather early epoch of wool and delaine printing, and have been replaced by simpler preparations.

Steam Colours upon Cotton.—In the opening paragraphs of this section of his work, De Vinant states that forty years ago steam colours were nearly unknown in Rouen, the printers then only worked blue and yellow, which were mixed to produce green. He relates that in 1873, when he was quite young, he worked in the laboratory of the Gobelins under Chevreul, where he made experiments upon steam colours for cottons, which he afterwards successfully carried out on the large scale with his father.

They prepared their jaconets with a double mordant of tin and alumina, and we have the extraordinary statement that their reds had for basis a mordant of bichloride of mercury, or corrosive sublimate.

In the period 1837—1845, he states that Paris had the monopoly of printing jaconets and batistes in madder colours; it was at this time that Broquette, a printer in Paris, improved the process of printing upon wool, and invented the method of printing with various lakes, and about the same time applied albumen as a vehicle for some colours; the Mulhouse printers are said to have infringed or employed Broquette's patents, and the inventor having proceeded against them before the legal tribunals, received damages or recompense to the extent of 60,000 to 80,000 francs, after

which they were allowed to continue to use his methods. It is only, he continues, since this time that Mulhouse acquired the reputation which it now so well deserves.*

With regard to Broquette's process of animalising cotton fabrics so as to receive colours like wool, we find the following receipt for the preparation of the cloth:—

3 lb. casein or lactarine, 18 lb. warm water; let steep together for several hours and add $1\frac{1}{4}$ lb. strong ammonia; twelve hours after the ammonia, add $2\frac{1}{2}$ gallons water and 3 lb. nitric acid at 10° Tw.; this causes a separation of the caseine which is washed with water, drained, and re-dissolved in ammonia and mixed with 7 lb. olive oil, the whole well mixed up. The pieces are padded in this mixture and dried, then steamed. Afterwards, without washing, the goods were prepared with stannate of soda and sulphuric acid in the usual way for steam colours.

This process of Broquette's we may add, for De Vinant says no more about it, was for a time thought to be a most valuable discovery, very beautiful results were obtained by it as far as colours go, but it was soon given up for two reasons, first, it was very expensive, costing 20 or 30 francs to prepare 100 metres of cloth; and secondly, it gave a stiffness and harshness to the cloth which was very objectionable. About 1850, the editor saw some work done upon delaines and cotton by Thomsons', of Clitheroe, by this process, and some by Koechlin's of Mulhouse, which were particularly rich, and had a softness of effect much resembling fine woollen goods in appearance, but they had a bad touch; the oil was used to soften the harshness given by the caseine, but it was only partially successful in accomplishing it, and in consequence the goods were not suitable for garments.

We select some of the steam colours as given by De Vinant for calico.

Black No. 1.— $1\frac{1}{4}$ gallon vinegar or acetic acid at 4° Tw.—1 gallon logwood liquor at 24° Tw.— $\frac{1}{2}$ pint bark liquor at 14° Tw.— $\frac{1}{2}$ gallon iron liquor at 22° Tw.— $\frac{1}{2}$ gallon red

* P. 471.

liquor at 14° Tw.—1 lb. oil—3½ lb. starch—1 lb. gum substitute.

Black No. 2.—1 gallon acetate of alumina at 14° Tw.—1½ gallons iron liquor at 13° Tw.—1 gallon acetic acid—3½ gallons logwood liquor at 8° Tw.—9 lb. starch—4 lb. gum substitute ; boil, and when cool add to each gallon of colour ¼ pint nitrate of iron.

Black No. 4.—This black is called English black, from the firm of Mr. Ed. Potter, Manchester.—1 gallon logwood liquor at 8° Tw.—½ pint caustic soda at 70° Tw.—1¼ lb. starch—½ oz. red prussiate ; boil, and when cool strain.

Chromium Black.—1 gallon logwood for purple at 14° Tw.—2 lb. starch—2 lb. British gum ; mix separately—8 lb. acetate of chromium below and 13 oz. carbonate of soda, stir until the effervescence is over, mix with the preceding, then add 1¼ gallon acetic acid strong, and 2 quarts acetic acid, boil and strain.

Acetate of Chromium for above Black.—75 lb. bichromate—100 lb. strong sulphuric acid—5½ gallons water, boiling ; add gradually 25 lb. white starch, when the action is over and the liquid cold ; add 285 lb. of acetate of lead, stir well and use the clear.

It is added that these blacks need not be steamed, a simple passage in bichromate with addition of carbonate of soda to preserve the whites, suffices to render the colour adherent to cotton goods. The bath may be made up of 100 gallons water—6 lb. bichromate of potash, and 3 lb. carbonate of soda.

Chocolate No. 5.—1 gallon redwood liquor, at 5° Tw.—½ gallon logwood liquor, at 5° Tw.—1¼ lb. starch—1 lb. gum substitute—10 oz. alum—5 oz. salammoniac. Boil, and when cold add 8 oz. nitrate of copper.

Chocolate No. 13, called English.—3¾ gallons sapan liquor, at 20° Tw.—2 gallons logwood liquor at 14° Tw.—1¾ gallons berry liquor at 11° Tw.—1¾ gallons nitrate of alumina, at 11° Tw.—24 lb. starch—1 quart oil—1¼ lb. chlorate of potash. Boil, and when cold add 2½ lb. prussiate of potash.

Nitrate of Alumina for the above.—7 pints water—3 lb. alum—3 lb. nitrate of lead.

Nitro-sulphate of Alumina.—4 gallons water—20 lb. nitrate of lead—15 lb. sulphate of alumina.

Chromium Chocolate.—10 gallons Lima extract, at 30° Tw.—3 gallons Cuba extract, at 30° Tw.—add 10 lb. crystals of soda to 10 gallons of acetate of chromium, and when the effervescence is over mix all with 19 gallons water—8 gallons acetic acid—22 lb. white starch—8 lb. gum substitute, and boil.

Dark Catechu.—1 gallon catechu liquor at 14° Tw.—4¼ lb. gum substitute—4 oz. salammoniac—when cold add 4 oz. nitrate of copper.

Dark Green, No. 49.—First part: 2½ gallons berry liquor, at 7° Tw.—8 lb. starch—2 lb. alum—5 pints acetate of alumina at 14° Tw.; boil. Second part: 1¼ gallon berry liquor, at 7° Tw.—12½ lb. yellow prussiate—3 quarts Lima and redwood at 14° Tw.; dissolve warm and add to the first part. Third part: 3 quarts of acetic acid—½ lb. oxalic acid—2 lb. bichloride of tin at 120° Tw.—6 lb. extract of indigo; mix, and add to the previous when cold.

Dark Green No. 53.—First part: 1 gallon berry liquor, at 10° Tw.—1 gallon bark liquor, at 14° Tw.—½ gallon logwood liquor, at 7° Tw.—½ gallon water—4 lb. starch; boil, and while hot add 2½ lb. alum; when cooler add 5 lb. prussiate of potash; when cold, 1 gallon prussiate of tin. Second part; ½ lb. starch—½ gallon water; boil, and add 12 oz. oxalic acid and 12 oz. tartaric acid; mix the two parts together.

Dark Blue.—2 gallons water—3½ lb. starch; boil, and add 6½ lb. prussiate of potash—6¼ lb. tartaric acid; when cooler add 6 oz. oxalic acid, and when cold add 8½ lb. prussiate of tin.

White Resist, for Steam Colours.—1 gallon boiling water—24 lb. gum; dissolve. 1¼ lb. resin soap—10 oz. carbonate of soda—1 gallon boiling water; dissolve. 20 lb. animal black, pure and fine—20 lb. carbonate of zinc—10 lb. chalk—3 gallons water. Mix the three solutions together.

White to Print upon Colours.—Albumen water, with gum water, and 4 lb. to 5 lb. of zinc white per gallon, with or without addition of a small quantity of ultramarine.

M. De Vinant states that the following colours were com-

municated to him by M. Mathias Paraf-Javal, of Thann, near Mulhouse. The preparation for the colours consisted in padding in strong stannate of soda, and afterwards passing in sulphuric acid.

Red, for Block or Roller.—3 quarts cochineal liquor, at 20° Tw.— $\frac{1}{4}$ pint bark liquor, at 30° Tw.—1 lb. starch; boil, and add immediately 6 oz. binocalate of potash, and when cold 12 oz. acetate of tin below.

Acetate of Tin.— $4\frac{1}{2}$ lb. tin crystals— $2\frac{1}{4}$ lb. bichloride of tin, at 110°—1 lb. 2 oz. acetate of lead, and 1 quart water; stir well, and use the clear.

Pink, to go with Red.—Standard: $\frac{1}{2}$ gallon cochineal liquor, at 7° Tw.—1 pint acetate of alumina, at 22° Tw.—6 oz. tartaric acid, at 30° Tw.— $2\frac{1}{2}$ lb. gum. For light pinks reduce this with 3 or 4 measures of gum water.

Green.— $\frac{3}{4}$ lb. starch— $\frac{1}{2}$ gallon water; boil, and add 4 lb. yellow prussiate— $\frac{1}{4}$ lb. red prussiate— $3\frac{1}{2}$ lb. tin; mix well, and add $\frac{1}{2}$ lb. chrome alum and 2 oz. acetic acid.

The above green has some resemblance in its composition to Havranek's green. It is directed to be reduced with starch paste for light shades.

Finishing of Steam Colours.—According to Vinant, steam colours on calico have no starch in the finishing, being simply dried up after washing; however, he finds that the best stiffening or finishing material is potato starch, at 1 lb. per gallon of water, with about 1 ounce of very white beef suet. Pass through the starching mangle hot, dry, and if required, calender. For bluing a small quantity of what is called English blue may be used.

Coloured Finish for Madder Foulards.—This is to give a yellowish tone to the ground. Boil $2\frac{1}{2}$ lb. quercitron bark for half-an-hour with 10 gallons water, filter, and add $2\frac{1}{2}$ gallons farina paste, at $1\frac{1}{8}$ lb. per gallon, and $\frac{1}{2}$ gallon acetate of alumina.

The next section of M. De Vinant's work treats of spirit colours (*couleurs d'application*), or that class of colours which resemble steam colours in composition, but are not steamed.

They form the lowest, because the loosest, class of colours employed in calico printing, and should never be employed for goods which are likely to require washing, they are only suitable for linings and similar articles. Since the extensive use of aniline colours in printing it has been found that many of these simply thickened with starch or gum answer the purpose of spirit colours; they are easy to print, regular in shade, and are not likely to tender the cloth, as many spirit colours may do unless carefully managed. The receipts for the old spirit colours in De Vinant do not present any special points of interest, and we pass them over to come to the next section, from which we extract some receipts for discharges—most of these will be new to colour mixers who have learned their business within the last dozen years, but familiar to the older ones. They may be looked upon as obsolete, but experience has shewn that some of those styles, thought to be for ever buried, come up again at times with some new face upon them and have a successful run. We shall therefore extract several of these discharges; it will be observed that some are for block.

White Discharge upon Manganese Bronze.—2 gallons water—5 lb. pipeclay—2½ lb. gum. Dissolve warm, and when cold add 4 to 6 lb. liquid muriate of tin.

Yellow Discharge on same.—2 gallons water—2 to 2½ lb. chromate of lead—2½ lb. starch. Boil, and when cooled add 1½ to 1¾ lb. crystals of tin.

Red Discharge on same.—2 gallons peachwood liquor at 8° Tw.—1¼ lb. alum—7½ lb. gum. While warm add 1 lb. tartaric acid—1 lb. oxalic acid—1 lb. crystals of tin.

Blue Discharge on same.—Add Prussian blue in paste to the white discharge in quantity necessary for the shade of blue required.

Green Discharge on same.—Mix equal proportions of the yellow and the blue discharge.

Chromate of Lead for Yellow Discharge.—5 lb. yellow chromate—2 gallons hot water—5 lb. acetate of lead—2 gallons hot water. Dissolve separately, mix together, and collect the precipitate.

White Discharge upon Chrome Orange.—1 gallon water— $3\frac{1}{2}$ lb. tartaric acid— $3\frac{1}{2}$ lb. oxalic acid—10 lb. pipeclay. Afterwards add 1 gallon thick gum water, and 5 lb. crystals of tin. It may be further thickened with gum substitute.

Red Discharge on Chrome Orange.—2 gallons peachwood liquor at 8° Tw.— $1\frac{1}{4}$ lb. oxymuriate of tin, thicken with gum, and add 5 oz. tin crystals and $1\frac{1}{4}$ lb. nitromuriate of tin.

Blue Discharge on Chrome Orange.—2 gallons hot water—2 lb. Prussian blue paste dissolved in muriatic acid—10 oz. tartaric acid—10 oz. oxalic acid— $1\frac{1}{4}$ lb. tin crystals—2 lb. starch; when cold add $1\frac{1}{4}$ lb. muriate of tin, or more if the colour does not discharge well.

Yellow Discharge on Chrome Orange.—1 gallon water—1 lb. starch; boil, and add $1\frac{1}{8}$ lb. nitric acid—8 oz. acetate of lead mixed.

Another Yellow Discharge.—This is simply nitrate of copper thickened; nitrate of alumina or other acid salts of this nature may also be used.

Lilac Discharge on Chrome Orange.—1 gallon logwood liquor at 4° Tw.—dissolve in it 1 lb. alum, thicken with starch, and when cold add $\frac{1}{2}$ lb. oxymuriate of tin and $\frac{1}{2}$ lb. nitromuriate of tin.

Purple Discharge on Madder Chocolate.—This kind of madder chocolate is obtained by first dyeing a purple in the usual way, and then padding over with iron buff, which changes it into a brown or chocolate. To obtain purple objects on the chocolate ground the buff is discharged by the following composition:—1 gallon boiling water— $1\frac{1}{4}$ lb. tartaric acid—1 lb. oxalic acid— $4\frac{1}{2}$ lb. gum substitute.

Pink Discharge on Madder Chocolate.—To about 1 gallon gum substitute add $1\frac{1}{4}$ lb. tin crystals and $\frac{1}{2}$ oz. sulphuric acid; to be printed upon the chocolate obtained as above; twenty-four hours after printing to be washed off in warm chalk and water, and then passed in alkali or soaped.

Orange Discharge upon Madder Purple.—This is rather a dark buff discharge than an orange. It is made by precipitating nitrate of iron with carbonate of soda, collecting the oxide of iron and dissolving it in a mixture of equal parts of

sulphuric and muriatic acid at 7° Tw. to saturation—2 gallons of this sulphomuriate of iron— $\frac{1}{2}$ gallon lime juice at 36° Tw.— $\frac{1}{2}$ lb. sulphate (? bisulphate) of potash, thickened with gum. This mixture printed on madder purple, aged in a warm room for forty-eight hours, and then passed into rather strong bleaching powder solution to discharge the purple and fix the buff.

[To be continued.]

Methyl Green on Woollen Yarn.—This is dyed by first mordanting in a mixture of hyposulphide of soda or hydrochloric acid, so as to induce a deposit of sulphur in the wool; about 1 lb. of hyposulphide and half a pound of acid to 3 lb. yarn. After the mordanting wash and dye in the solution near the boiling point. To obtain yellower shades picric acid is added.

7. *Note upon the Prussiates of Aniline.**

BY M. WEHRLIN.

TOWARDS the end of 1863 M. H. Cordillot discovered an aniline black made by means of prussiate of ammonia (ferricyanide), which could be fixed by steaming. It was the first black which had been obtained without the use of salts of copper. After being given up for a length of time it came into use again when the extract style was introduced, which required a good black fixing by steam.

Up to the present time (1874), the principal blacks employed were by means of yellow or red prussiate of potash, or the corresponding salts of ammonia. M. Camille Koechlin has communicated to me the receipt of a very fine black obtained by the direct action of ferricyanic acid upon aniline; unfortunately, this black does not keep good beyond a few hours, and is difficult to use. In the various blacks I am

* Bull. de la Soc. Ind. de Mulhouse, xliv., p. 386.

about to speak of, whatever salt may be employed it always produces either the ferro- or the ferricyanide of aniline.

I have endeavoured to isolate these two salts, and have succeeded in obtaining them in a pure crystallized state.

Ferrocyanhydrate of Aniline.—This corresponds to the yellow prussiate, and is made by acting upon aniline with ferrocyanic acid. The great difficulty is to obtain the acid in a sufficiently concentrated state to dissolve enough aniline. The simplest process of preparing the acid is that proposed by M. Kuhlmann, of Lille, which consists in decomposing the ferrocyanide of barium by sulphuric acid; but, not having a sufficient quantity of the barium salt, I employed the following process, more practical in a printworks :—

A solution of yellow prussiate of potash is made and another of tartaric acid, they are gradually mixed, pouring the acid into the prussiate, a precipitate of bitartrate of potash takes place, and the hydroferrocyanic acid remains in solution. The strongest acid which I procured by this method marked 36° Tw., and serves to dissolve the aniline. In dissolving the aniline care must be taken not to let the temperature pass 120° F., as an excess of aniline interferes with the crystallization the liquid is preferably left slightly acid; upon cooling it forms abundant crystals of prussiate or ferrocyanide of aniline.

This salt crystallizes in white plates, very light. When quickly dried at the ordinary temperature they remain white for a considerable time, but become yellow when dried at 120° F., and turn black in time even in stoppered bottles.

The ferrocyanide is very soluble in both cold and warm water; when the solution is boiled it decomposes into ferricyanic acid and aniline, which floats upon the surface of the liquid. It is but slightly soluble in alcohol, ether, or sulphide of carbon, but dissolves readily in aldehyde. It can be purified by two or three times recrystallizing, but prepared in this way it cannot be obtained wholly free from bitartrate of potash.

By adding salammoniac and chlorate of potash to a thickened solution of this salt, very fine blacks can be obtained

by steaming without the necessity of ageing. The colour prints well, does not act upon the doctor, nor tender the cloth; it keeps good for eight days or upwards.

When the black colour is reduced by thickening, it gives good greys, which are fast to soap and chlorine. Intense blacks can also be obtained by mixing the ferrocyanide with a thickened solution of chlorate of aniline.

The blacks from the ferrocyanide do not become green in the air as the copper blacks do. They can be printed with albumen colours, such as pigment green or ultramarine, or with alizarine, and extract colours without forming white edges; they work well also with steam Prussian blues or greens. They may be boiled in soap and strongly colored just as the ordinary black.

This salt mixed with steam logwood black increases its intensity and fastness, and a steam colour may be thus prepared which can be printed in the finest patterns, preserving its goodness under albumen and extract colours.

A solution of prussiate of aniline thickened with gum substitute gives, after twenty-four hours ageing and passing in bichromate, tolerably fast greys; the same colour steamed gives a bright blue like Prussian blue, but not fast to soap.

Ferricyanide of Aniline.—This is prepared in the same way as the ferrocyanide, substituting red prussiate for yellow prussiate, the hydroferricyanic acid can be obtained at from 35° to 40° Tw.; it dissolves aniline more readily than the other acid. The crystallized salt is in plates of dark violet colour; it is very soluble in cold or warm water, it dissolves in alcohol and aldehyde with a violet colour, not soluble in ether or sulphide of carbon, and is richer in aniline than the ferrocyanide.

The salt gives very fine blacks in the same way as the ferrocyanide, the same preparations yielding a more intense colour. The colour does not hurt the cloth nor act upon the doctor, but it does not keep as well as the previous colour.

*8. Note upon the Prussiate of Aniline.**

BY M. ERNEST SCHLUMBERGER.

M. WEHRLIN having communicated to me his notes upon the prussiates of aniline, and having myself worked upon the same subject, I desire to append the following observations:—

The ferrocyanide of aniline being but sparingly soluble, its saturated cold solution not marking more than 4° or 5° Tw., I thought this property could be advantageously made use of in its preparation. After some trials it was found that the best results could be obtained by the decomposition of muriate of aniline with yellow prussiate of potash. The prussiate of aniline on account of its sparing solubility precipitates almost completely, while the chloride of potassium, which is soluble in three times its weight of water remains dissolved.

I operate in the following manner:—Four pounds aniline are mixed with 4 lb. muriatic acid at 29° Tw., and the mixture left until completely cold; on the other hand, 4¾ lb. of yellow prussiate are dissolved in 8½ lb. of boiling water, the latter solution is allowed cool to 134° F., and just before it would begin to crystallize it is poured into the cold solution of muriate of aniline. Upon cooling of the whole there is obtained a semifluid mass of crystals of the prussiate of aniline. For use I find it sufficient to let the mass drain well upon a filter, because drying is difficult to accomplish on a quantity without decomposing a part of the salt. The foregoing quantities yield about 9½ lb. of drained salt.

This process appears to me simpler, quicker, and cheaper than the one described by M. Wehrin.

The moist salt can be kept without decomposing for several days, especially if in a dark place; light causes it to become violet coloured. After a while it is completely decomposed; a sample which I prepared two years ago was found recently

* Abridged from the Bull. de la Soc. Ind. de Mulhouse, xlv., p. 390.

to be changed into a black, earthy substance, probably a mixture of aniline black and Prussian blue; but for several days at least it can be calculated upon as keeping good.

To make a black colour, about 10 per cent. of the prussiate of aniline is added to a thickened solution of chlorate of aniline.

In endeavouring to prepare the ferricyanide of aniline in a similar manner from red prussiate, I found the result unsatisfactory on account of the greater solubility of the salt in water.

I have serious doubts of the value of M. Wehrin's process for preparing this latter salt, for the decomposition of red prussiate by an equivalent of tartaric acid is very incomplete; the solution would contain besides hydroferricyanic acid a large proportion of tartaric acid and potash, which would naturally interfere with the subsequent reactions.

Moreover, I have found the ferrocyanide preferable in all respects to ferricyanide. The chief objection to this statement is that it is not rational to employ a compound in the colour which must consume a certain portion of the oxidizing power of the chlorate of potash before it could itself act as an oxidizer. But this objection is more apparent than real, for in the case of copper or iron blacks the same may be said. The sulphide of copper must be first oxidized before it can act, and the salts of iron at the minimum of oxidation must go through the same change, and they can be used without inconvenience.

The quantity of chlorate of potash required to oxidize 100 of yellow prussiate is moreover not more than 4.9 parts, and the use of chlorate of aniline permits the introduction of as much chlorate as may be required. On the other hand, the ferrocyanide colour keeps for an indefinite length of time and does not act upon the doctors, which is not the case with the ferricyanide. There is no exaggeration in saying that the colour prepared with the ferrocyanide of aniline is as much superior to the old aniline colours with red prussiate, as the sulphide of copper black is superior to Lightfoot's original colour.

M. Brandt was requested to report upon these two papers ; his report is in great measure an echo of the papers themselves. It appears that so long ago as 1866, M. Risler-Beunat, of Barcelona, forwarded a note to the Industrial Society of Mulhouse, describing a steam aniline black made with muriate of aniline, chlorate of potash, and a large proportion of prussiate of copper. But this black was found to tender the cloth, and, moreover, required ageing before steaming, which brought it down to the level of the common aniline blacks, most of which can be steamed after ageing. M. Brandt considers Schlumberger's process for preparing the ferrocyanide of aniline as decidedly preferable to Wehrin's, but declines to decide as to the relative excellence of the two prussiates for making the colour—some manipulators will prefer one and some another. He concludes as follows :—

“Up to the present time either the ferro- or ferricyanic acid, under one form or another, form part of the composition of all steam aniline blacks. This consideration leads us back to the first aniline black in which the prussiates were used, that is the one discovered by M. Cordillot, who employed the prussiate of ammonia. It was not a steam black, but at the same time it was the starting point of all the blacks with prussiate, and by modifying the preparation could be made into an excellent steam black. In order that Cordillot's original black should develop without steaming, the colour was required to be very acid and to be aged very warm ; with all that it was not an intense black, being too blue, and much inferior in every respect to the sulphide of copper black which displaced it. But if instead of a black to be developed by ageing, a steam aniline black had been wanted, it would have been found long since. In fact, by using a mixture of chlorate of aniline, prussiate of ammonia, and muriate of aniline, a very intense steam black can be obtained which yields to no other black, unless it be in cost, where Schlumberger's has the advantage.”

9. COLLECTED RECEIPTS.*

Colours for Woollen and Mixed Goods—Delaines.

For several years previously to 1852 delaine printing was a brisk and profitable business in Lancashire and elsewhere; about that time it suddenly fell off, whether owing to change of taste as some suppose, or as others think from the introduction of dyed alpaca goods it is unnecessary to discuss. In the United States it formed an important item in printing for several years after it had become quite insignificant in England. It has been suggested to the editor that there are symptoms of a revival of the demand for printed woollens and delaines, and that it might be useful to a younger generation of colourists to see a collection of authentic receipts of colours which were successfully used for these styles some years ago.

Printing of fine woollens has never been much practised in the North of England, not working in well with the staple business of a calico printer. The fabric technically known as "delaine," or more fully "muslin," or "mousseline-de-laine," is, as is well known, composed of a cotton warp and a woollen weft. The relative weight of wool to cotton varies in different qualities, an average cloth gave three-fifths wool to two-fifths cotton. The chief point in delaine printing is to obtain the same shade upon the cotton as upon the wool, or at least so nearly alike in shade as not to give the appearance of "threadiness" which arises from an unequal dyeing of the fibre. Both pure woollens and delaines are prepared with tin for printing by processes which have been previously given. Black colours were given vol. i., pp. 23 and 108, and are not repeated in this collection.

The following receipts are from unpublished documents; they are first hand from different sources; many of them have been applied by the editor in practice, and the others are from reliable correspondents who have given permission for

* Continued from vol. ii., p. 96.

their publication. It cannot be too often repeated that a collection of receipts is like a collection of tools, only to be profitably used by those who understand how to use them; the ignorant, or the inexpert will make nothing out of them, and will probably say the tools are bad to excuse their own want of skill. Even an expert colourist getting a new and genuine receipt from a friend will often find he cannot obtain good results from it until he has made some change or modification to adapt it to his particular wants or circumstances.

No. 169. Outline Chocolate.—Delaine.

18 gallons logwood liquor at 12° Tw.—6 gallons bark liquor at 16° Tw.—40 lb. starch—10 lb. gum substitute; boil and cool to 150° F. 7½ lb. alum—3 lb. chlorate of potash—3 lb. red prussiate.

No. 170. Dark Chocolate.—Delaine.

3 quarts sapan wood at 12° Tw.—5 quarts logwood liquor at 12°—2 quarts nitrate of alumina—1½ quarts bark liquor at 24°—4 lb. starch—4 lb. British gum—1 gill oil; boil, cool, and add 4 oz. chlorate of potash—4 oz. yellow prussiate—4 oz. tartaric acid.

No. 171. Chocolate for Wool.

12 quarts archil liquor at 18° Tw.—1½ lb. alum—4 oz. salammoniac—4½ oz. oxalic acid; stir until the effervescence is over—2½ lb. starch—2¼ lb. gum substitute—14 oz. sulphate of indigo. A small quantity of black for wool may be added to obtain darker shades.

No. 172. Blotch Chocolate for Wool.

10 quarts archil—1 quart water—6 oz. sulphate of indigo; thicken with 4 lb. gum.

No. 173. Blotch Chocolate.—Delaine.

10 quarts peachwood liquor at 24° Tw.—30 lb. gum—4 quarts hot water—7½ lb. alum dissolved in 14 quarts hot water—1½ quarts bark liquor at 30°—2 quarts logwood liquor at 30°—3¾ lb. muriate of copper and 2 lb. salammoniac.*

* It is to be noted that these receipts where the logwood and other liquors are so strong as 30° Tw., are of French origin. Liquors of such strength, though preferred on the continent, are seldom prepared in England.

No. 174. Gum Red Chocolate.—Delaine.

10 gallons sapan liquor at 14° Tw.—40 lb. gum substitute, dissolve by heating—½ lb. salammoniac—6 lb. alum—2¼ lb. chlorate of potash—4 oz. oxalic acid—7 quarts prepared logwood liquor, which is made by dissolving 9 lb. alum—9 lb. red prussiate—2½ gallons lime juice in 12 gallons of logwood liquor at 12° Tw.

No. 175. Another Gum Red Chocolate.—Delaine.

24 lb. gum—8 quarts sapan liquor at 30° Tw.—4 quarts water—8 quarts nitrate of alumina—2 quarts bark liquor at 30°—1½ quarts logwood liquor at 30°—1¾ lb. chlorate of potash—7 oz. sulphate of copper; the two latter salts dissolved in 6 quarts boiling water. The nitrate of alumina made from 8 quarts boiling water—8 lb. alum—11 lb. nitrate of lead.

No. 176. Catechu Brown Blotch.—Delaine.

2 gallons catechu liquor at 5 lb. per gallon—2 gallons gum water—1¼ lb. copper solution. Copper solution made by dissolving 8 lb. acetate of copper—2 lb. cream of tartar—12 lb. acetic acid—2 gallons water, using the clear.

No. 177. Dark Brown.—Delaine.

Catechu standard made by dissolving 2½ lb. of catechu in a gallon of bark liquor. Red standard made by dissolving 1 lb. alum—4 oz. oxalic acid—7 oz. chlorate of potash in 8 lb. sapan liquor at 16° Tw. Purple or blue standard, the prepared logwood liquor in No. 174 above. A standard brown may be prepared by thickening with gum substitute a mixture of 5 parts red standard, 40 parts catechu standard, and 10 parts of the prepared logwood.

No. 178. Brown.—Delaine.

3 gallons bark liquor at 16° Tw.—1 gallon sapan liquor at 10° Tw.—1 quart logwood liquor at 10° Tw.—6 quarts red liquor at 16° Tw.—3 pints nitrate of alumina—2½ lb. alum—2 oz. chlorate of potash—2 oz. tin crystals—7 lb. starch; boil, and add 2 oz. oxalic acid.

[To be continued.]

10. British and Foreign Patents, from the Commissioners of Patents Journal, August 28th to September 28th, 1877, inclusive.

Bleaching, Cleansing, Scouring.

1900. ADOLPHE ALEXANDRE PLANTROU, jeune, of Boulevard de Strasbourg, 23, Paris (France), Director of Manufacture, for an invention of "An improved process of scouring and purifying vegetable and animal fibres and fabrics."—Dated 15th May, 1877.
3235. ALEXANDER MELVILLE CLARK, of 53, Chancery Lane, in the county of Middlesex, Patent Agent, for an invention of "Improvements in decolorizing textile and other materials."—A communication to him from abroad by Joseph Marie Clément, of Paris, France.—Dated 5th August, 1877.
3617. JOHN IMRAY, of 20, Southampton Buildings, in the county of Middlesex, for an invention of "Improvements in the bleaching and cleansing of textile vegetable materials."—A communication to him from abroad by Paul Bayle, Merchant, and Rinaldo Pontiggia, Chemist, both of Paris, France.—Dated 27th September, 1877.
- 42,670. A. A. PLANTROU, a Patent of Improvement for "Scouring and purifying textile substances at once."—Dated 23rd July, 1877.—(Original Patent, 14th May, 1877.—Belgian Patent.
- 42,895. J. M. CLÉMENT, for an imported invention of "Improvements in decolouring vegetable and animal textiles."—Dated 24th August, 1877.—(French Patent, 28th July, 1877.)—Belgian Patent.

Patterns, Designs.

3123. EDWIN THURMAND, of Batley, in the county of York, for the invention of "An improved method of forming patterns or designs on felted fabrics."—Provisional protection has been granted.
4880. W. WINTER, of Prague, for "A process for obtaining photographic designs on fabrics."—5 years.—Dated 17th April, 1877.—Saxony Patent.

74. W. WINTER, of Prague, for "Obtaining photographic pictures on fabrics."—1 year.—(Secret.)—Dated 14th May, 1877.—Austrian Patent.

Colouring Matters.

- 188,061. FELIX DE LALANDE, of Paris, France, for the "Processes of obtaining artificial purpurine from alizarine."—Application filed 7th June, 1876.—United States patent.
- 188,217. JUSTUS WOLFF, of Wyke, near Bradford, and RALPH BETLEY, of Wigan, England, for "Processes of making dyes from naphthaline."—Application filed 23rd January, 1877.—United States patent.
- 189,538. JUSTUS WOLFF, of Wyke, near Bradford, and RALPH BETLEY, of Wigan, England, for "Production of coloring matters from aniline."—Application filed 23rd January, 1877.—United States patent.
76. M. E. SAVIGNY, of St. Mandé, and A. C. COLLINÉAU, of Paris, for "Obtaining an innocuous vegetable dye called 'cauline,'"—1 year.—(Secret.)—Dated 4th April, 1877.—Austrian patent.
- 42,602. J. ZELTNER, for "Obtaining a new colour called 'Ultramarine violet.'"—Dated 11th July, 1877.—Belgian patent.
- 42,603. J. ZELTNER, for "Obtaining a new colour called 'Ultramarine red.'"—Dated 11th July, 1877.—Belgian patent.
- 42,973. A. C. BEGHIN, for an imported invention of "Composition of a new black."—Dated 30th August, 1877.—(French patent, 1st May, 1877.)—Belgian patent.

Printing and Dyeing Processes and Apparatus.

1648. GEORGE CANTRELL GIBBS, of Brentford, in the county of Middlesex, has given notice to proceed in respect of the invention of "Improvements in machinery or apparatus for dyeing and colouring felt, silk, and other textile or porous fabrics."
1761. JOSEPH WILSON SWAN, of Newcastle-on-Tyne, in the county of the same town, Chemist, and ISAAC FREEMAN, of the same place, Accountant, have given notice to proceed in respect of the invention of "Improvements in the means of printing from punctured stencils."
2513. WILLIAM MORGAN-BROWN, of the firm of Brandon and Morgan-Brown, Engineers and Patent Agents, of 38, South-

- ampton Buildings, London, and 1, Rue Laffitte, Paris, for an invention of "Improvements in printing textile fabrics."—A communication to him from abroad by Henry Dorr Dupee, of Boston, county of Suffolk, state of Massachusetts, United States of America.—Dated 29th June, 1877.
3214. GEORGE CANTRELL GIBBS, of Brentford, in the county of Middlesex, for an invention of "Improvements in machinery or apparatus for dyeing and colouring felt, silk, and other textile or porous materials."—Dated 19th September, 1874.—The £50 stamp duty has been paid.
2462. THOMAS NESHAM KIRKHAM, of West Brompton, VERNON FRANCIS ENSOM of Highgate, both in the county of Middlesex, and GEORGE SPENCE, of Pendleton, in the county of Lancaster, for an invention of "Improvements in apparatus suitable for scouring, washing, bleaching, dyeing, and drying fibrous materials in the raw and manufactured state, and for like purposes."—Dated 12th September, 1870.—This patent has become void.
- 188,370. WILLIAM IRELAND, of Buckhaven, North Britain, for "Machines for printing textile fabrics."—Application filed 1st May, 1875.—United States patent.
- 189,868. C. MCBURNEY, of Boston, Mass., for "Blankets for calico-printing."—Application filed 7th April, 1876.—United States patent.
- 189,371. WM. MATHER, of Salford, England, for "An apparatus for steaming and ageing printed fabrics."—Dated 25th November, 1876.—United States patent.
58. C. SCHOLZ, of Semil, for "An apparatus for applying colours on printing blocks."—1 year.—(Secret.)—Dated 14th May, 1877.—Austrian patent.

Yarn Treatments.

3427. JOHN COLLINS, of Glasgow, in the county of Lanark, North Britain, Engineer, for an invention of "Improvements in washing, scouring, and dyeing yarns, and in machinery or apparatus employed therefor."—Dated 11th September, 1877.
3488. JULIEN PATY, of Boulevard-de-Strasbourg, 23, Manufacturer, for an invention of "An improved apparatus for dressing or preparing yarns or materials in the process of colouring or dyeing wool, cotton, silk, and other fibrous substances."—Dated 17th September, 1877.—Provisional protection has been granted.

2982. ALBERT SAUVEE, of 22, Parliament Street, Westminster, in the county of Middlesex, Civil Engineer, for an invention of "Improvements in the apparatus used for dyeing materials, either woven, spun, or in skeins or hanks."—A communication to him from abroad by Monsieur César Corron, Dyer, of Saint Etienne (Loire), France.—Dated 1st September, 1874.—This patent has become void.
4996. W. VOGEL, of Chemnitz, for "Obtaining undyed plain and mixed worsted yarn from native dark sheep's wool."—5 years.—Dated 27th June, 1877.—Saxony patent.

Silk and Wool Treatments.

- 187,643. J. H. KNOWLES, J. K. PROCTOR, and F. P. PENDLETON, Philadelphia, Pa., assigns to said Proctor and Pendleton and Thomas Cunningham, Lucian Brown, George Brown, and H. B. Lincoln, of the same place, for "Wool-washing machines."—Application filed 16th October, 1873.—United States patent.
- 188,385. O. LOWE, of Hyde Park, Mass., for "Machines for cleansing wool and other material."—Application filed 31st July, 1876.—United States patent.
95. A. VOLKENBORN, of Langenberg, for "An apparatus for smoothing and lustring silk threads."—3 years.—Dated 20th June, 1877.—Prussian patent.
- 42,663. A. and V. and J. T. TRIBUILLET, of Brussels, a Patent of Improvement for "Processes and apparatus for washing wool, &c."—Dated 21st July, 1877.—(Original patent, 24 July, 1876).—Belgian patent.
- 42,820. Mrs. O. FREZON, Mrs. T. MACE, O. G. FREZON, E. A. PICARD, and Mrs. PICARD, for an imported invention of "Burling fancy coloured tissues."—Dated 14th August 1877.—(French patent, 11th August, 1877).—Belgian patent.
- 42,878. H. DEMEUSE and Co., for "Improvements in apparatus for burring wool."—Dated 21st August, 1877.—Belgian patent.

Finishing, Plaiting, and Miscellaneous.

1066. SAMUEL MILNE SMITH, CHARLES TELFORD SMITH, and WILLIAM BINNS, of the firm of Samuel Smith and Company, of Bradford, in the county of York, Dyers and Finishers, for an invention of "Improvements in finishing 'moreens' and corded fabrics."—Dated 16th March, 1877.—Sealed September 15th, 1877.

3293. GERARD WENZESLAUS VON NAWROCKI, of the firm of J. Brandt and G. W. von Nawrocki, Civil Engineers and Patent Agents, of 2, Koch Strasse, Berlin, in the German empire, for an invention of "An improved apparatus for testing the strength of cloth and other textile fabrics."—A communication to him from Hermann Ehlers, of Rostock, in the German empire.—Dated 29th August, 1877.—Provisional protection has been granted.
3451. BARKLY CHARLES WILSON, of the firm of Wilson, Collet, and Company, of the city of London, Lace Manufacturers, for an invention of "Improvements in machinery or apparatus for plaiting fabrics."—Dated 13th September, 1877.
3628. WILLIAM EDWARD NEWTON, of the office for Patents, 66, Chancery Lane, in the county of Middlesex, Civil Engineer, for an invention of "Improvements in machinery or apparatus for stretching fabrics."—A communication to him from abroad by Alfred Francois Lacassaigne, of Paris, in the republic of France.—Dated 27th September, 1877.
2873. JOHN HENRY JOHNSON, of 47, Lincoln's Inn Fields, in the county of Middlesex, Gentleman, for an invention of "Improvements in machinery or apparatus for folding or plaiting fabrics."—A communication to him from abroad by Orange McConnell Chamberlain, of the city, county, and state of New York, United States of America.—Dated 20th August, 1874.—This Patent has become void.
- 189,030. T. HAGERTY, of Brooklyn, N.Y., for "Plaiting-machines."—Application filed 6th March, 1877.—United States Patent.
- 42,599. D. PIRARD, of Brussels, for "A plaiting machine."—Dated 9th July, 1877.—Belgian Patent.
- 42,961. H. EHLERS, for "An apparatus for testing the strength of cloth."—Dated 30th August, 1877.—Belgian patent.
4855. H. EHLERS, of Rostock, for "An apparatus for ascertaining the strength of fabrics."—5 years.—Dated 12th January, 1877.—Saxony patent.
165. W. HEDTMANN and A. HENKELS, of Langerfeld, for "A plaiting machine."—3 years.—Dated 27th June, 1877.—Prussian patent.
277. J. MACDONALD, of London, for "A process for giving vegetable textiles a silky appearance."—3 years.—Dated 30th June, 1877.—Prussian patent.

THE TEXTILE COLOURIST.

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[Vol. IV.]

*I. Testing of Indigo.**

BY M. V. TANTIN.

IT is not necessary to dwell upon the importance it is to the consumer of indigo to be able to ascertain the quality of what he purchases and employs. Every kind and every brand is subject to great variations; it is therefore indispensable for the user to have a ready method of exactly testing the amount of colouring matter in this dyestuff.

The external character, though of importance, may be very deceptive, and however experienced the purchaser, he must be aware that he is liable to very erroneous conclusions if he values a sample of indigo from its brand or its appearance.

When I first turned my attention to testing indigo, I expected to find some satisfactory method among those described in chemical works, but I was greatly deceived, for I could find no process which was at the same time accurate and easy to execute. The volumetric processes, founded upon the property of the colouring matter of indigo to be destroyed by various oxidizing substances, such as chlorine, bleaching powder, chlorate or bichromate of potash, are all subject to considerable error, for the oxygen does not act only upon the blue colouring matter, but also upon other organic substances present, such as the indigo brown, indigo

* Paper read to the Industrial Society of Flers (Orne). Abridged from *Moniteur Scientifique* for November, 1877, p. 1148.

gluten, indigo red, etc. Bichromate of potash, which has been specially recommended, has another inconvenience, that of making the liquids green, which causes it to be very difficult to determine the point of completion of the reaction.

The method of Houton-Labillardière rests upon a rigorously exact system, but his colorimeter does not shew in a clear manner changes of colour, and it is easy to make an error of 10 per cent. with it. The new and improved colorimeter of Salleron is, however, free from the defects of the old instrument, and enables the observer to discern very small differences of intensity of colour in the indigo solutions, so that a quantity of colouring matter inappreciable by means of the most delicate balance, can be estimated by means of this instrument. With this improved colorimeter, the method of Houton-Labillardière can be carried out; this principle is, that two solutions formed with equal weights of the same colouring matter in equal quantities of water, when viewed in glass tubes of the same diameter, will present colours of equal intensity, and that solutions made with unequal weights of the same colouring matter will exhibit colours with intensities proportionate to the quantities.

To estimate the difference in the intensity of coloured liquids, they are introduced into tubes graduated to the same scale, and placed in the apparatus called the colorimeter; then the more intensely coloured liquid is diluted with water until it is brought to the same shade as the less intensely coloured liquid, and the relative strength of the colouring matter calculated.

The new colorimeter of Salleron consists of a box in form of a truncated pyramid, fixed by one of its sides to a support, by which it can be raised or lowered at will; the broader end of the box is shaped so that the face of the observer can be applied to it and shut out the greater part of the exterior light; inside the apparatus is provided with a pair of blackened metallic plates, in each of which are cut two parallel slits of the same dimensions, a hinged mirror of opal glass reflects diffused light into the interior of the box. Between the two metallic plates there is a glass cell con-

structed of two pieces of glass, separated by three glass partitions of equal size, two at the ends and one at the middle, forming two separate cells of rectangular section. Above the box is fitted a graduated burette which holds water; there is also attached a platinum tube which descends to the bottom of the glass cell, the upper part being connected with an india-rubber tube, so that by blowing through it the bubbles of air cause the liquid in that cell to be thoroughly mixed up.

Method of Proceeding.—To prepare the sample to be tested, the indigo sent by the dealer is scraped by a knife until 5 grammes (about 75 grains) are detached. If the sample consists of several pieces a portion must be scraped off each one, proportional to its weight.

The scraped indigo is ground in an iron mortar and sieved through fine sieving silk. The grinding and sieving must be continued until all has gone through the sieve, for if any portion is left it is impossible to be certain that a fair sample has been taken.

A quantity of the sieved indigo, equal to 0.3 gramme (about 5 grs.) is weighed out very accurately upon a sensitive balance.

As a standard for comparison, pure indigotine is taken. This is procured by collecting the scum or flower which continually forms on the top of indigo vats. This scum is treated by hydrochloric acid and water to remove foreign substances. The residue of this operation carefully washed upon a filter is dried or kept in well-stoppered bottles.

The comparison of samples of indigo with this indigotine requires much attention; it can only be used to determine the value of some given sample of indigo, which in its turn serves as a standard with which to compare other samples.

Solution of the Indigo Samples.—The 0.3 gramme of indigo is introduced into a test tube; 10 grammes of broken glass, quite clean and dry, are added, and then by means of a graduated pipette, 5 c. centimetres (about 75 grains measure) of chemically pure sulphuric acid added. I attach much importance to the use of this acid in preference to the Nordhausen sulphuric acid, which gives purple-coloured solutions in which

the eye appreciates with great difficulty small variations of intensity.

The tubes are heated to 140° or 160° F., in a water bath, stirring the contents every half hour. At the end of four hours the solution of the indigotine will be complete, and is mixed with water so as to make three litres; to do this accurately the experimenter must be provided with a narrow-necked flask of that capacity, with a mark on the neck at the right point. The solution is left to settle for half an hour before being examined in the colorimeter.

Comparison of Intensity of Colour.—Ten cubic centimetres (about 150 grs.) of the solution to be tested is then transferred to the glass cell on the right hand, and an equal quantity of the standard liquid is placed in the left hand cell. The two solutions will be generally found of different intensity, the standard being most frequently the darkest. By means of the burette a few drops of water are added to the left hand cell, then by means of the india-rubber tube air is gently blown into the liquid, so as to mix it well up with the water added. The two solutions are now observed, to see if they are of equal depth, if not so, more water is carefully added until the two solutions are exactly equal. The operation is then finished. The burette shews how many c. centimetres of water have been added, and the calculations can then be made.

If we suppose that it has been necessary to add 2 c. centimetres of water to the standard liquor to make it of equal shade with the sample, it is evident that the colouring power of the standard will be to that of the sample as 10 plus 2, that is, 12 is to 10, or the sample is worth five-sixths of the price of the standard. If the standard has an actual value of 20 francs the kilogramme, the sample is only worth five-sixths of that price, or 16 francs 66 centimes.

The reverse of this might happen; the sample might give a darker colour than the standard; in such a case the liquids must be placed in the contrary cells (the burette being a fixture), and the sample solution diluted until the colours are equal. Supposing it had been necessary to add $1\frac{8}{10}$ c. centimetre of water to the sample, then the colouring power of the

sample would be to the standard as 11.8 is to 10; again, taking the value of the standard as 20 francs per kilogramme, that of the sample would be 23 francs 60 centimes.

A glance at the following table will immediately shew the differences there are between the selling prices and the actual value of various kinds of indigo as calculated by the real amount of colouring matter present. Attention may be directed to the first four samples of indigo, which are Bengal and of the same brand. It will be seen that the fourth when compared with the first shews an advantage of 11 per cent. to the purchaser.

Several of the indigos put down in the table were employed on the large scale, and the results in practice were in perfect agreement with the results of analysis.

It is necessary in order to have absolutely exact results, that the comparison should be made between indigos of the same origin, because it is evident, for example, that with an equal proportion of indigotine Bengal indigo would be of higher value than a Java or Guatemela indigo.

[In the foregoing paper M. Tantin appears to have obtained good results from the peculiar form of colorimeter employed, but we do not think it well to let the paper pass without saying that this method of testing indigo or any other colouring matter is open to numerous sources of error, and can only succeed in the hands of a very expert manipulator accustomed to the apparatus. With regard to indigo, the method is particularly liable to error from the influence which foreign matters have upon the colour of the sulphuric solution. The 10 c. centimetres put into the glass cells represent a very small quantity of indigo, less than one-fiftieth part of a grain, and the utmost delicacy must be used to avoid considerable errors. As to the supposed percentage of indigotine in the samples, the figures are worthless except for comparison. The *pure indigotine* cannot be obtained by the method described; if the product contained 80 per cent. of indigotine it would probably be the utmost. Only crystallized indigotine can be considered as pure.—*Ed.*]

RESULTS OF INDIGO TESTING MADE AT THE INDUSTRIAL SCHOOL OF FLERS (ORNE), IN 1875.

<i>Kind of Indigo.</i>	<i>Indigotine per cent.</i>	<i>Selling price per kilo.</i>	<i>Actual value per kilo.</i>
Various brands of Bengal.	63·66	21·30	22·58
	63·66	21·50	22·58
	59·57	22·00	21·13
	56·43	21·30	20·02
	59·02	20·20	20·04
	62·27	19·80	22·00
	55·00	19·40	19·50
	64·34	22·40	22·82
	71·41	28·00	25·33
67·85	22·60	24·07	
Madras	39·07	12·50
Java	67·05	20·00
Vellore.....	44·46	14·00
Kurpah	61·27	14·00
Oude	47·08	16·50
Native	48·36	15·00
Guatemala	65·62	21·70
Colombia.....	72·70	25·20
Nicaragua	64·34	18·00

—◆—

Raves Black.—This black, called “noir direct,” was patented in France April 19th, 1877, No. 112,497. It is described as obtained by acting upon a decoction of campeachy with a salt or mordant which changes the colour to black; the precipitate is washed and delivered to be consumed in the state of paste.—*Bull. de la Soc. Chem., Oct. 5th, 1877.*

2. *Materials for a History of Textile Colouring, No. 8.*

The Introduction of Chloring by Machine.—This improvement is of modern date, and the only authentic documents referring to it consist of a communication from MM. Claude Royet and Georges Steinbach to the Industrial Society of Mulhouse, read October 31st, 1855, and a report of the Chemical Section of that Society upon the said communication. They are translated in the following pages from the 27th Volume of the Bulletin of the Society.

“Everyone familiar with the production of madder and garancine styles is acquainted with the numerous irregularities arising from the system of clearing whites by grassing. In winter it is especially difficult to obtain regular results, sometimes for weeks together the goods cannot be put upon the grass; we need not speak of the cost of labour, loss of time, and various accidents occasioned by the wind, and soot from the works, chimneys, etc.

“Chemists and manufacturers have doubtless always had a view to chlorine as a means of bleaching independent of climatic influences. But this element, so powerful and so valuable in general bleaching, is not easy to manage, and it has required considerable labour and experiment to enable the operators to guide and control at will its powerful bleaching properties.

“The problem to be solved in the application of chlorine was apparently simple, being no more than to clear or bleach the unprinted portions of the cloth without materially affecting the colours.

“During the winter of 1846-1847, the firm of Blech, Steinbach, and Mantz, undertook an extensive series of trials to resolve the question. The experiments made at this time may be classified in six series.

“(1) Printing, padding, or covering by means of a pin

roller (*mille points*) the print with solution of bleaching powder at various strengths, commencing with a standard at 11° Tw., mixed with water in the proportion of 1 to 1,000, 1 to 125, 1 to 40, 1 to 20, 1 to 4, 1 to 2, and passing the goods immediately into boiling water for three minutes.

“(2) Padding with the same roller and same solutions as in No. 1, and passing the goods directly afterwards into a drying room heated to 120° F.

“(3) Padding as in No. 1 with pin roller and drying upon steam drums or tins.

“(4) Padding as in No. 1 and immediately steaming for three minutes.

“(5) After padding in various strengths of bleaching powder as in No. 1, leaving wet on rolls for twenty-four hours, then washing in hot water.

“(6) After padding as in No. 1, passing into water acidulated with tartaric acid at the rate of 1 lb. to 40 gallons of water.

“The series of trials from 1 to 6 were repeated in the same manner with the neutral chlorides of potash and soda in various proportions, employing also an ordinary padding machine instead of the engraved roller.

“For several months we practised padding the goods in weak chloride of lime and drying slowly in the ‘hot flue,’ but by this method we could get through only a limited number of pieces, and we were obliged to give it up for the system of using the pin roller, and drying immediately by passing the cloth over an extended surface of steam chests. This method, which we applied on the large scale in our works since the spring of 1847, has yielded constant good results.

“Later on this plan spread to other works in France, Germany, and England, and if we are correctly informed, one or two English firms clear their garancine styles precisely according to the No. 4 method above, that is, applying the bleaching liquor by means of a roller, and steaming immediately afterwards. This system of working, however, has not given us good results, the fine, delicate, and detached parts of the design being considerably injured by it.

“Chlorine has been employed for many years past in print-

works for bleaching grey calico, the whites of madder purples, for oxidizing wool, etc., its manner of action being always the same, that is, sometimes acting as a dehydrogenizing agent, removing hydrogen from colouring bodies and transforming them into other substances, sometimes acting as an oxidizing agent, taking the hydrogen of water and liberating its oxygen. In the special case of garancines its action is not thoroughly complete, for it may be observed that the white grounds—though seemingly perfectly bleached—become slightly pink when rinsed in water. The question arises whether there is only temporary destruction of some part of the colouring matter which revives upon contact with water and air.

“A similar phenomenon is observable in the discharge white upon Turkey red, which becomes yellow after a time of exposure to the air; but here the question is probably complicated on account of the presence of a strongly resinous matter.

“In clearing garancine dyed goods there is a fortunate circumstance which permits the operation to be carried on with remarkable regularity. It may be observed that the unprinted parts take up liquid more easily than the printed parts, and, consequently, the bleaching solution acts more vigorously upon the whites than upon the colours. This peculiarity of the mordanted portions not being wetted so easily as the unmordanted parts makes it practicable to treat catechu grounds, logwood blacks, cochineal scarlets, and other colours, which it would be impossible to treat in a liquid bath of bleaching powder, however weak, without greatly injuring the colours. This peculiarity is not, however, an essential property; it does not explain how it is that the whites of garancine work cannot be properly cleared in the usual clearing beck. It will be seen further on that the difference in the manner of acting of the bleaching agent by padding, or by solution, or as we may say by printing, or by dyeing methods, rests entirely upon the relative proportions of the substance applied and the liberty of action which the two different processes allow. By printing it is possible to regulate the strength of the solution according to the requirements of the whites. Working in a solution is

different under any circumstances, for the goods are entirely surrounded by the medium, and the destructive action of the chlorine cannot be confined to a given place as it can by printing. This difference, which is apparently physical, and in one case may be said to be putting the chlorine on the cloth, and in the other putting the cloth in the chlorine, is found upon examination to possess chemical aspects which make the two processes quite distinct, and which shew that the advantages of direct application of the bleaching liquor arise from the fact that by immersion in chlorine the active element is not uniformly absorbed by the whole surface of the cloth, but that the coloured parts take the greater portion of it; the organic substances of the colour shewing an attraction for it similar to that of mordants for colouring matter. The actual substance of the fabric, the cotton, taking only an insignificant proportion, so that if the oxidizable matter which may remain in the mordants be neglected, the action is one simply between the colouring matter and the chlorine.

“This fundamental distinction is easy to verify, and shews itself most plainly in working at low temperatures.

“For example, in the cold the decomposition of the colouring matter, combined with the mordants, is effected before there is any action upon the cloth, and this decomposition is capable of destroying twenty times the amount of chlorine which is required to clear the whites by the system of padding, whence comes the possible destruction of the colours themselves before the whites are cleared.

“By working warm with bleaching solution, the chlorine, which is much more readily separated in that state, acts with but little difference upon all organic matters present, and experience shews that there is an approach to uniform action all over the surface, and no disproportionate absorption by the coloured parts.

“When the same quantity of chlorine is applied by the liquid or dyeing process to dyed colours, which is found sufficient to give good whites by the padding or printing process, nothing is found to take place beyond an oxidizing action, and it requires twice or three times the amount of chlorine

before it begins to act upon the whites, and then the action is found to be accompanied by injury to the colours themselves.

"By whatever method the chlorine is applied to clear the whites it acts upon the colours themselves, when of equal permeability, before it acts upon the unmordanted parts; we understand by this that layer of crude colouring matter visible upon the white parts which, on account of its fineness, has mechanically penetrated the pores or interstices of the cloth. The pure isolated colouring matter is, on the contrary, attacked more powerfully than the colouring matter combined with mordant.

"On account of its chemical properties, as well as from its practical importance, the method of chloring practised by our firm has become not only unique, but also the only one capable of giving good whites upon unsoaped work, or with colours which will not stand soaping.

"We have communicated this statement, because for some time past we have heard the credit of this discovery attributed to various printers, and we wished to shew that our establishment was the first to employ it on the large scale, and that it was the result of trials which occupied a considerable time before it was perfected.

"If we did not patent this process at the time of its discovery, it was simply because we adhered to the broad and liberal traditions of Mulhousien industry."

The Chemical Section made a short report upon this paper, which was presented by Dr. Penot, and runs as follows:—

"All manufacturers know how difficult it was always, and sometimes impossible, especially in winter, to obtain good whites in garancine work. It was very rarely that perfect whites could be obtained by laying out on the grass, and the serious objections of time, labour, tears by wind, stains from soot, etc., were not to be overcome. Of late years this slow and imperfect process has been replaced by a chemical method, rapid, certain, and economical, which has effected quite a revolution in this branch of the printing business.

Chloride of lime, which has already been of such important help in the art, is the agent employed.

“After dyeing in garancine the pieces are padded, with a pin roller, in a solution of chloride of lime, and then immediately dried over steam chests. The mordanted parts of the print do not readily absorb the solution, while the unmordanted parts become, on the contrary, impregnated with the chloride of lime, and are bleached in a regular manner; the same process can be employed with advantage for catechu grounds, logwood blacks, and cochineal scarlets, which could not be submitted to a bath of liquid chloride of lime without injury to the colours. This new process is, therefore, of considerable importance, and is the only one which can be used for obtaining whites on unsoaped work or work which does not stand soaping.

“It is a novel and important application of chlorine, added to those others which had been indicated by Berthollet and by our venerable colleague, M. Daniel Koechlin. Messrs. Georges Steinbach and Royet claim the honour of this discovery for their establishment, where it has been employed on the large scale since the spring of 1847. There were some doubts expressed relating to the priority of this new invention. It was known that this method of clearing with chloride of lime had extended to several works in Alsace and other places, in consequence of instructions supplied by M. Gustave Schwartz, of the firm of Schwartz-Huguenin. After a long discussion, in which the two parties interested took part, it was unanimously decided by the Chemical Section, including MM. Gustave Schwartz, Georges Steinbach, and Royet, that the firm of Blech, Steinbach, and Mantz was the first to employ chloring by printing for the purpose of clearing whites; but on the other side it was acknowledged that the firm of Schwartz-Huguenin had discovered and employed the same process at very nearly the same time, and that some months later M. Gustave Schwartz communicated it to Ecks', at Cernay, and Dollfus-Mieg's, of Mulhouse, who immediately applied the system, whence it gradually spread to other works in Alsace and abroad.”

Combination of Bleaching Powder and Acids for Clearing.—

The following article and the criticism upon it are from the 28th volume of the "Mulhouse Bulletin," p. 418; the paper which comes first was read by M. Henri A. Koechlin, at the meeting held December 30th, 1857:—

"At the present time the chloring of garancine styles has generally replaced grassing both in France and other countries.

"The chloring, with very few exceptions, is done by padding with engraved roller in chloride of lime, soda, or potash, at various strengths, from $\frac{1}{2}^{\circ}$ to 3° B., according to the engraving of the roller and the kind of dyeing employed, the pieces being immediately submitted to the action of heat, which liberates a portion of the chlorine.

"In some establishments the pieces are dried upon the usual drying cylinders; in this case a small padding apparatus is placed before the drying machine, composed of two rollers, one of which is engraved, and the other acting as a pressure roller. In most works the chloring is effected by the printing machine, and the drying accomplished either in hot chambers, with currents of heated air, or upon steam chests.

"In the heated air arrangement it frequently happens that the atmosphere is so completely saturated with humidity that the goods are with difficulty dried.

"This inconvenience, which causes loss of time and labour, because the speed has to be reduced, induced me in the winter of 1854 to try cold chloring, by which I obtained good results. In this process I replace the action of heat by the action of an acid; that is, I decompose the chloride of lime or soda by an acid, forming with it a soluble salt, the chlorine is liberated, which then acts as a bleaching agent upon the parts in contact with it.

"I print with two pin rollers or fine stripes, the first with the chloride of lime or soda at $\frac{1}{2}^{\circ}$ to 1° B., according to the strength of the engraving, and the second with acetic, hydrochloric, or sulphuric acid.

"The quantity of acid should be calculated from the strength of the chloride employed, and the quantity of liquid which is

communicated to the cloth. One pound dry chloride of lime requires 1·2 lb. commercial acetic acid, 1·8 lb. hydrochloric acid at 20° B., and 0·8 lb. of strong sulphuric acid.

“The piece is delivered by the machine without drying, and is immediately passed into water and washed.

“To determine the strength of the acid and water necessary for a given strength of chloride of lime it is sufficient to determine the proportion between the quantity of acid liquid furnished by the acid roller and the bleaching liquor furnished by the chlorine roller.

“Taking all the circumstances into consideration, this cold chloring is not more expensive than the ordinary process, for though the cost of drugs is greater, it presents the following advantages :—

“(1) A weaker chlorine solution suffices.

“(2) There is less labour.

“(3) It does not require a printing machine with its drying, but a simple padding apparatus with two rollers.

“(4) It permits the chloring of more pieces in the same time.

“(5) By using hydrochloric or acetic acid for the decomposition of the chloride of lime, a soluble salt of lime is produced which can be completely removed by washing, which is an advantage in case certain colours have to be blocked in afterwards.

“(6) The white remains purer and does not become yellow as is frequently the case in common chloring, when it is necessary to chlorine strongly, or when the piece is more strongly heated than is necessary to dry off the water which it contains.

“In this method of chloring the acids used must be free from iron when red or catechu colours are to be cleared, the presence of this metal turns the reds brown and darkens the catechu.”

The following report upon this paper was prepared by M. C. Royet, and adopted by the Chemical Section of the Society.

"M. Henri A. Koechlin's process of chloring garancine dyed prints consists essentially in replacing the action of heat by the action of acids. It requires a two-colour printing machine, the first pin roller gives chlorine to the piece, the second pin roller covers it with acidulated water in proportions suitable for the decomposition of the chloride of lime. After the printing, and without drying, the pieces are washed.

"Before proceeding to try this method of chloring I ascertained the proportions of liquid furnished to the cloth by each of the rollers which I used. I found the first roller supplied 15 litres of water to 300 metres of calico, and the second only 10 litres; these quantities will vary as the engraving becomes used up, and should be again determined from time to time, and also when re-engraved.

"One litre of our bleaching powder solution at 8° B. (about 11° Tw.) requires generally 100 grammes of hydrochloric acid at 19° B. to saturate it.

"I only experimented with the ordinary hydrochloric acid, acetic acid being too costly, and sulphuric acid difficult to manage, giving rise to the slightly soluble sulphate of lime, which an imperfect washing would leave in the fibres.

"I made 50 trials with small samples of prints, using chloride of lime at various dilutions from $\frac{1}{8}$ to $\frac{1}{128}$, with a single pin roller, and drying, and the same number of trials with two rollers, employing acid of proper strength, as indicated by the chloride of lime and the furnishing of the rollers.

"In every case the samples chlored by the new process were inferior in the whites to those done by the old method—the greater the proportion of acid the worse the whites appeared.

"This result seems surprising; but it is known with what slowness solutions of madder are acted upon by chlorine, as can be seen any day in the clearing becks by the old system. These becks keep their colour for several hours, though containing more chlorine than is necessary for their bleaching. If, then, in chloring, the decomposition of the chloride is hastened

so that it will be accomplished in less time than it requires to act upon the alizarine, it may happen that an excessive addition of acid will produce worse whites. A great portion of the chlorine seems to escape without acting upon the colouring matter. This explanation of the phenomenon appears to be supported by the results of all the trials made upon lengths of about half a yard.

“But in experimenting upon a length of 300 metres, passing the cloth through the two-colour machine and rolling the pieces on themselves at once, and then afterwards taking off and washing, the whites are as good as by the dry method.

“We may observe—

“(1) That in chloring by roller the drying has never been an obstacle, where the stoves or heated rooms were properly constructed and sufficiently ventilated.

“(2) That if at the present time the chloring by engraved roller is only used exceptionally, as for steam colours, it is to avoid the cost of labour, lappings, back greys, etc.

“(3) In chloring by padding, followed by drying upon a steam drum or upon Tulpin's machine, an intelligent youth can very well manage the apparatus.

“(4) If it is desired to effect the chloring without drying, the action of steam can replace the use of acids. In this way chloring is carried on in several works, the pieces being padded in the bleaching liquor, then passing through a steam box furnished with guiding rollers and washed.

“From a chemical point of view, therefore, the process of M. Henri A. Koechlin has no advantages. The delicacy of the manipulation more than outweighs the economy effected by not drying; further, we may state that this system of chloring acts particularly upon purples, which become ‘rusty,’ or ‘foxy,’ even when only half the required proportion of acid is used. Steam colours, and other styles which do not permit of rolling up in the wet state, cannot be treated by this method.”

3. COLLECTED RECEIPTS.*

No. 179. Dark Grey.—Delaine.

2 quarts gum water—1 pint lilac standard below—4 oz. prussiate of potash—3 gills of acetate of indigo. Lilac standard is prepared from 4 quarts of logwood liquor at 30° Tw.—8 quarts red liquor at 18° Tw.—1¼ lb. oxalic acid dissolved in 2 quarts hot water—1¼ lb. salammoniac—10 oz. acetate of copper dissolved in 2 quarts hot water. Light greys can be obtained by reducing with gum water.

No. 180. Pearl Grey.—Delaine.

3½ quarts gum water—1 pint lilac standard above—2¼ oz. yellow prussiate dissolved in 1 quart water—¼ pint bark liquor—¼ pint acetate of indigo.

No. 181. Cocoa Brown.—Delaine.

A logwood solution, made by steeping 3 lb. of ground logwood for several hours in hot red liquor, is used under the name of lavender standard in the following receipt :—1 gallon cochineal liquor at 8° Tw.—4 gallons berry liquor at 12° Tw.—24 gallons lavender standard—thicken with gum substitute and add 3 lb. alum—6 oz. cream of tartar—2½ lb. tartaric acid.

As a general rule the numerous shades which contain all the three elementary colours considerably diluted, and which constitute the almost infinite greys, drabs, stones, etc., are seldom directly prepared from their constituents, but are obtained by mixing other colours together. Each colourist has his own system of standards for preparing the compound shades, and it cannot be said that there is any particular method which can be strongly recommended above others, at the same time it is impossible to go into the details of these colours without giving the composition of a great number of standards, which seems unnecessary.

* Continued from p. 195.

No. 182. Blue for Grounds.—Delaine.

4½ lb. prussiate of potash—4 quarts hot water—4½ lb. tartaric acid, mix and draw off the clear, which is to be made into 6 quarts by washing—6 lb. gum—1½ quarts prussiate of tin—1½ lb. tartaric acid—2 oz. oxalic acid.

No. 183. Dark Blue.—Delaine or Muslin.

2 lb. prussiate—1 lb. tartaric acid—1 oz. salammoniac—2 oz. oxalic acid—1 oz. sulphuric acid—1 gallon water, hot; mix, dissolve and let settle; take the clear only—1 gallon clear liquor from the preceding—2 lb. starch—1 pint tin pulp.

No. 184. Dark Blue.—Delaine.

6½ gallons water—14 lb. starch—3 lb. salammoniac; boil and cool to 150° F., and add 33 lb. tartaric acid—2½ lb. ground oxalic acid—6 gallons tin pulp; mix well and add 20 lb. yellow prussiate—10 lb. red prussiate.

No. 185. Dark Blue.—Delaine.

9 gallons water—1½ lb. salammoniac—14 lb. starch; boil and add 20 lb. tartaric acid—3 lb. oxalic acid—7 gallons tin pulp; mix well and add 13 lb. yellow prussiate—6½ lb. red prussiate.

No. 186. Gum Blue.

6½ gallons soluble gum water, hot—3 lb. salammoniac—30 lb. tartaric acid—4 lb. oxalic acid—6 gallons tin pulp—18 lb. yellow prussiate—10 lb. red prussiate—8 lb. extract of indigo.

No. 187. Dark Blue.—Delaine.

1 gallon water—2 lb. starch; boil well and add 10 oz. salammoniac—2 lb. 10 oz. yellow prussiate—1 lb. 5 oz. red prussiate—3 lb. tartaric acid—1 gallon tin pulp.

No. 188. Crimson.—Delaine.

Ammoniacal cochineal liquor made as follows:—50 lb. cochineal—60 lb. strong ammonia; steep 24 hours, then add 6½ gallons boiling water; stir and strain, pressing out the liquid; wash the grains with 6½ gallons more of hot water, and strain and press; make up the liquor to 19 gallons. Keep the liquor hot in a water bath with stirring to expel

some of the excess of ammonia, then thicken with dry gum senegal, and add 16 lb. alum—4 lb. tartaric acid.

No. 189. Pink.—Delaine.

Use the same ammoniacal cochineal as in the last receipt, expel the free ammonia rather more completely than is necessary for crimson, thicken with dry gum, and add 14 lb. alum—14 lb. cream of tartar—1 lb. oxalic acid; reduce to depth required by gum water.

No. 190. Pink Standard.—Delaine.

11 lb. cochineal—22 lb. ammonia—4½ gallons water—1¼ lb. cream of tartar; boil for 40 minutes, strain and add 8 oz. alum per gallon and thicken with gum senegal.

No. 191. Red.—Delaine.

6 pints cochineal liquor at 7° Tw.—1 pint berry liquor at 12° Tw.—10 oz. starch; boil and add 3½ oz. oxalic acid—3½ oz. tin crystals. For a darker red use the cochineal liquor stronger.

No. 192. Dark Red.—Delaine.

16 gallons cochineal liquor at 16° Tw.—35 lb. starch—3 lb. oil or fat—boil well and cool with stirring; when at 150° F. add 7 lb. crystals of tin—7 lb. oxalic acid.

No. 193. Scarlet.—Delaine.

The red No. 191 is actually a scarlet on account of the berry liquor; but better scarlets can be made upon the basis of the No. 192 colour, though more expensive; not more than one part of berry liquor for twenty parts of cochineal should be used with a colour containing so much free acid unless a decidedly yellow shade is aimed at.

No. 194. Green.—Delaine.

Green colours are mixtures of blue and yellow, and admit of great variety in modes of preparation, the most usual way being to have two or more standard green colours, bluish and yellowish, and mixing these in the proportions required for the shade wanted. The following examples are sufficient for illustration:—9 gallons berry liquor at 16° Tw.—70 lb. soluble gum—dissolve and add 11½ lb. alum—5½ lb. oxalic

acid—4 gallons red liquor at 18° Tw.—5 gallons soluble gum water—30 lb. yellow prussiate—4 gallons extract of indigo— $\frac{1}{2}$ gallon acetic acid. This may be called a gum green; a paste green may be prepared as follows:—4 gallons berry liquor at 16° Tw.—5 gallons water—30 lb. starch, boil and add 6 lb. alum—3 lb. oxalic acid—2 gallons red liquor at 18° Tw.—15 lb. yellow prussiate—2 gallons indigo extract.

No. 195. Dark Green.—Delaine.

1 gallon water—7 gallons bark liquor at 18° Tw.—13 lb. starch—4 lb. gum substitute—5 lb. alum—1 lb. crystals of tin—14 lb. tartaric acid—14 lb. prussiate of potash—1 lb. oxalic acid in 1 quart hot water— $\frac{1}{2}$ gallon extract of indigo.

No. 196. Dark Green.—Delaine.

7 quarts bark liquor at 18° Tw.—1 quart red liquor at 18° Tw.—3 lb. starch—2 lb. tin pulp—3 lb. tartaric acid—3 lb. prussiate of potash—4 oz. oxalic acid in 1 pint hot water—1 quart extract of indigo.

No. 197. Light Green.—Delaine.

6 pints berry liquor at 10° Tw.—8 oz. alum—2 lb. gum substitute, boil and add 1 lb. extract of indigo, and when cold 6 pints of the following blue part:—7 lb. yellow prussiate—2 lb. alum—12 oz. oxalic acid—2 gallons hot water, mix. In a separate vessel mix very well $\frac{1}{2}$ pint of muriate of tin at 120° Tw. with two gallons gum water, and add to the prussiate liquor, stirring very well.

No. 198. Buff.—Delaine.

$3\frac{1}{4}$ gallons berry liquor at 6° Tw.— $2\frac{1}{2}$ gallons cochineal liquor at 8° Tw.— $1\frac{1}{2}$ gallons red liquor at 18° Tw.—4 lb. alum—2 lb. oxalic acid. This standard is to be mixed with senegal or substitute gum water, according to shade required, say 1 of standard to 4 or 6 of gum water.

No. 199. Yellow.—Delaine.

18 gallons berry liquor at 16° Tw.—10 lb. crystals of tin, to which add gradually $3\frac{1}{2}$ lb. soda crystals; when the effervescence is over mix with 10 lb. starch and boil well.

No. 200. Orange.—Delaine.

Orange colours are made from yellow and red in different proportions, according to the depth and hue required; equal proportions may be employed for dark orange, and as much as 20 parts of yellow to 1 part of red for a yellow orange. The red No. 192 may be used.

*4. M. Michel de Vinant on Dyeing, Printing, and Bleaching.**

M. DE VINANT gives other discharges of the same nature. It may be observed here that many of the effects obtained some thirty or forty years ago upon madder colours by various after treatments of discharging and dyeing in other materials to produce various effects were relinquished because they could be tolerably well imitated with cheaper dyestuffs, though not of course of so permanent a nature. The continually increasing price of madder was one reason why it could no longer be used so freely in combinations with styles which were not of the first class nor commanding the best price. But madder now in the shape of alizarine is as cheap as ever it was, and it might not be amiss that attention should be directed to the getting up of some modifications of the obsolete styles in which madder entered as a conspicuous element. Turkey red, for example, can now be dyed at a price which would probably make it available for some of the discharge styles formerly in vogue. The following are illustrations of the composition of the old discharges for Turkey red taken from De Vinant; most of them it will be observed are only fitted for block printing, but the composition and thickening could be easily modified to suit roller printing.

Discharge Black on Turkey Red.— $\frac{1}{2}$ lb. Prussian blue No.

* Continued from vol. iv., p. 187.

4 below—1 lb. acetic acid—1 oz. nitric acid ; leave together twenty-four hours, and grind well ; add $\frac{1}{2}$ lb. water— $\frac{1}{4}$ lb. starch ; boil, and when cold add a few drops of muriate of tin. It will be observed that this is not a black at all, it is simply a spirit blue, which, being printed on the red and not having sufficient acid to give it discharging powers, gives rise to what may pass for a black. At present aniline black is used as a black in the discharge style, and also some logwood blacks, notably the so-called spermaceti black, which, from its fatty character, is for a time capable of keeping out the chloride of lime.

Prussian Blue No. 4.—1 lb. Berlin or Chinese blue— $\frac{3}{4}$ lb. hydrochloric acid ; heat to dissolve, then precipitate by a large quantity of water and filter down to a thick paste.

White Discharge on Turkey Red.—1 gallon water— $7\frac{1}{2}$ lb. gum ; dissolve and add $1\frac{1}{4}$ lb. tartaric acid and $7\frac{1}{2}$ lb. pipeclay.

Another White Discharge.— $1\frac{3}{4}$ gallons water— $3\frac{3}{4}$ lb. gum senegal— $1\frac{1}{4}$ lb. tartaric acid— $1\frac{1}{4}$ to 2 lb. oxalic acid—10 lb. pipeclay— $2\frac{1}{4}$ lb. muriate of tin.

Blue Discharge on Turkey Red.— $1\frac{3}{4}$ gallons of water thickened with salep or tragacanth—5 lb. tartaric acid— $2\frac{1}{2}$ lb. oxalic acid— $1\frac{3}{4}$ lb. Prussian blue No. 4—1 lb. muriate of tin.

Yellow Discharge on Turkey Red.—2 gallons water— $3\frac{3}{4}$ lb. starch—20 lb. nitrate of lead— $2\frac{1}{2}$ lb. tartaric acid. After discharging, the yellow to be raised in bichromate of potash slightly acidulated with acetic acid.

All these colours are to be discharged by means of bleaching powder. They require three or four minutes in a tolerably strong liquor containing the bottoms, and are then passed into water and washed.

Discharge for Light Purple Mordant.—2 gallons lime juice at $1\frac{1}{2}^{\circ}$ Tw.—6 oz. bisulphate of potash. Thicken with 10 lb. gum substitute at 100° F.

Discharge for Blacks.—2 gallons lime juice at 10° Tw.—

6 oz. tartaric acid—6 oz. bisulphate of potash. Thicken with 10 lb. gum substitute.

These discharges are to be dried in a hot room, and washed off twenty-four hours afterwards in cow dung with chalk.

Catechu Brown Resist for Madder and Garancine Styles.—4 gallons lime juice at 30° Tw.—35 lb. gum—4 gallons catechu liquor at 22° Tw.—2 lb. acetate of copper—1 lb. salammoniac—5 lb. arseniate of potash. Dissolve at a gentle heat and strain.

Resist for Catechu.—(Tartrate of Chromium).—6 lb. bichromate of potash—1 gallon boiling water, add by degrees 9 lb. tartaric acid dissolved in 8 lb. water—1¼ gallons water hot, 2½ lb. arseniate of potash—4 lb. potash. Dissolve separately, mix the two liquids, and thicken with gum substitute (if for black add pipeclay), and add 4 lb. olive oil.

Passing on from this section our author gives a number of various colours and processes which seem thrown together without any order or system. We select receipts for some colours which have become nearly forgotten from disuse; no one knows when some of them may be revived in new styles, and it is well to preserve an account of them. The following refer to some applications of indigo:—

Fast Green for Shirtings.—3 gallons of water—5 lb. white starch, boil and add 3 gallons of water containing 20 lb. nitrate of lead thickened with 30 lb. of starch gum; when cold add 5 gallons of precipitated blue below, and 5 lb. syrup of sugar or molasses. Print the colour the same day it is made, and as soon after as practicable fix in a cistern provided with rollers and containing milk of lime, wash and wince in cold and weak solution of bleaching powder; wash well and then chrome to bring up the yellow part.

Precipitated Blue.—15 lb. caustic soda at 40° Tw.—7½ lb. ground indigo in pulp containing 2½ lb. of dry indigo; add gradually 3¾ lb. tin crystals, heat to 140° F., cool and put into a vessel, then precipitate with 7½ lb. muriatic acid mixed with 1¼ lb. muriate of tin; filter and drain, wash with ½ gallon water mixed with ¼ lb. molasses. Repeat the wash-

ing three times, and keep the pasty mass covered up out of contact with the air. This colour should only be prepared as it is wanted, being injured by keeping.

Fast Green with Quercitron Yellow.—The indigo pulp is prepared by grinding $2\frac{1}{2}$ lb. indigo with $6\frac{1}{4}$ lb. water. The colour is made from 1 gallon caustic liquor at 22° Tw.— $1\frac{1}{4}$ lb. potash— $3\frac{3}{4}$ lb. slacked lime in the state of powder, which has been passed through a fine sieve— $3\frac{3}{4}$ lb. of the indigo pulp— $1\frac{1}{4}$ lb. orpiment— $3\frac{3}{4}$ lb. aluminate of soda. Heat to 100° F. for an hour, and thicken with starch gum (British gum). Two hours after printing pass in lime and water as for the preceding colour; wash well, and dye in quercitron bark, with addition of size to preserve the whites. If the whites are not good after dyeing soap lightly.

Aluminate of Soda for above.—5 lb. alum— $2\frac{1}{2}$ gallons water; dissolve and precipitate with 1 gallon of caustic soda at 26° Tw., collect the precipitate and wash it three times with 15 gallons of water, drain and dissolve in 1 gallon caustic alkali at 26° Tw. Use the aluminate at 26° Tw.

Another Fast Green.—Proceed as in the last receipt but one so far as dissolving the indigo, and filter the liquid; in the warm liquor dissolve 5 lb. nitrate of lead and 10 lb. starch gum, heat up to about 100° and add $\frac{1}{2}$ gallon wood acid or acetic acid at 11° Tw., and $\frac{1}{2}$ gallon acetate of tin at 16° Tw.; strain, print soon afterwards, raise in lime, and afterwards in chrome for the yellow. The acetate of tin is prepared by dissolving paste of oxide of tin precipitated from salt of tin by carbonate of soda.

Fast Blue for Shirtings.—In an iron boiler, five times the size required to hold the quantity of colour operated upon, take $3\frac{1}{2}$ gallons of caustic soda at 40° Tw., add $3\frac{1}{4}$ lb. of the paste of oxide of tin, heat to 120° F., stirring with a wooden spatula, and gradually mix about 2 lb. ground indigo; keep stirred for several hours and then cover up the boiler. Twelve or fifteen hours afterwards, heat up to 120° F., and add by degrees $7\frac{1}{2}$ lb. oxalic acid dissolved in a gallon of boiling water, stir well and leave at rest for two or three hours, covering the liquor up to keep it warm; draw off 2

gallons of the still warm yellow liquid and add to the rest 1 ½ gallons gum water, strain through a fine sieve, print, fix in lime the same day as printed, and oxidize but without chroming.

Another Fast Blue.—Mix 1 part of the precipitate blue with ½ part of protonitrate of iron, and thicken with dry gum. The protonitrate of iron is made by mixing equal parts of sulphate of iron (green copperas) and nitrate of lead, and taking the clear. After printing hang twelve hours in a warm room, then pass in a strong lime vat, wash, and sour; this colour may be lightly soaped. In rinsing in lime there will probably be formed a blue scum floating on the surface of the liquor, this must be removed or kept from contact with the cloth, as it will give stains. If the colour “marks off” in the lime, it is a sign that it has not been hung long enough.



Aniline Blue.—Jeannelles' patent for substituting aniline for indigo in dyeing fibres of vegetable or animal origin, woven or unwoven, is abstracted in the Bulletin of the Chemical Society of Paris for October 5th, 1877, as follows:—The principle of the process is the oxidation of aniline salts in very weak solutions, the materials to be dyed being present. The proportions for 100 lb. of cotton are given as

Aniline	5 lb.
Muriatic acid.....	3 lb.
Sulphuric acid	12 lb.
Bichromate of potash	5 lb.

The muriate of aniline is first formed by mixing the aniline and muriatic acid, the bichromate is dissolved separately and the whole diluted with cold water to about 100 gallons.

The cotton is worked in the liquor for about an hour, then washed, and passed into a slightly alkaline bath heated to 100° F. The dyed colour is directed to be finally topped with ordinary aniline blue, or preferably by a short dipping in a weak indigo vat.

5. *Abridgments of Complete Specifications of Patents Recently Published.*

A.D. 1877, February 20th.—No. 698.

ALSTON, JOHN STIRLING, and REID, WILLIAM. "Improvements in Apparatus to be used in connection with various Processes of Treating Yarns with Liquids."

The following is the provisional specification of the patent; the full specification refers to three sheets of drawings accompanying; it is published at 8d.

"This invention has for its object the constructing and arranging of apparatus for treating yarns with liquids in an improved manner, and so that the yarns may be subjected to less handling and less risk of injury than in the apparatus ordinarily used for the same purposes.

"The present invention is also to a certain extent an improvement on or addition to that described in the Specification of Letters Patent obtained by William Reid, one of the present applicants, and dated 23 September 1875 (No. 3319).

"The apparatus for expressing liquids from yarns, described in the said earlier specification, has been found to be practically successful and useful in many applications, and may be advantageously combined with some of the improved apparatus constituting the present invention; but in some applications it is believed that the improved liquid expressing apparatus, hereafter described, will be found more convenient and advantageous.

"In one modification of liquid expressing apparatus comprised in the present invention there is a stationary flat plate, covered or coated with blanket, felt, rubber, or other suitable material, and on this plate several hanks of saturated yarn distended by two rods are laid. A movable upper or pressing plate working in or on guides, and having its under side coated with rubber or other suitable material, is arranged over the stationary plate, and is brought down by means of revolving cranks, eccentrics, or cams, or by means of levers or

of hydraulic or steam cylinders, so as to exert on the yarns the pressure necessary for expressing the liquid. An arrangement of endless chains similar to that described in the earlier specification, herein-before referred to, is to be employed for conveying the yarns to and laying them on the stationary plate, and for conveying them away therefrom; and such chains may be moved by hand, or a suitable intermittent motion may be imparted to them from an eccentric or crank on one of the revolving shafts of the machine.

"In a second modification, the upper or pressing plate is the same as in the first modification; but the lower plate is made movable horizontally, and receives the yarns upon it when it is moved out from under the upper or pressing plate. In both modifications the plates may be curved instead of flat if found preferable.

"In a modification of yarn saturating apparatus which will work automatically and conveniently in combination with the second modification of liquid expressing apparatus herein-before described, and which is advantageously adapted for immersing and working yarns in dyeing or other liquids. The tank or vessel is by preference of a nearly semi-cylindrical form, and has working in connection with it a wheel fitted with two sets of spokes or arms, and mounted on a horizontal shaft, situated by preference a little above the level of the liquid in the tank. On each arm there are two hooks placed at a distance apart, suited to the length of the hanks of yarn, and as each pair of arms comes round and downwards at one side of the tank, the attendant worker places on them several hanks of yarn. The hanks are distended on two rods, and are placed on the wheel by engaging the rods on the hooks on the wheel arms, the rods being parallel to the shaft, and the hanks being held radially.

"Alternate forward and backward motions are given to the wheel by any suitable gearing, the forward motions being greater than the backward motions, so that whilst the alternate motions cause the yarn to be well worked in the liquid, the quantity on each pair of wheel arms is gradually moved round through the liquid to the side opposite that at

which it was put on the wheel. The lower plate of the liquid expressing arms is moved under a quantity of yarn hanks, just as the forward motion of the wheel arms lifts them above the level of the plate, and then the next backward movement of the wheel arms lowers the hanks with their rods upon the plate, the rods becoming disengaged from the hooks on the wheel arms, and the plate being moved away from the wheel before the arms rise again.

“After the lot of yarns have been pressed, they are prevented from returning with the lower plate by the further rod being held so that the plate moves out from under the hanks, and allows them to fall upon rails or other supports, from which they can be removed by hand or by endless chains or by other suitable mechanism.

“In a second modification of yarn saturating apparatus which may be more suitable than the first for some dyeing or similar processes a rectangular tank is employed, and the yarn hanks are hung on transverse horizontal rods which are moved in succession from one end of the tank to the other by endless chains. The rods have toothed or plain wheels on one or both of their ends, so as to receive rotatory motion from fixed or reciprocating racks or bars at the sides of the tank; and the rods have boards or paddles fixed to them at the parts on which the hanks hang, such boards or paddles projecting to one side of the rods so as to have a swaying and increased action in turning over the yarn hanks.

“In a third modification of yarn saturating apparatus suitable for some dyeing or similar processes, the hanks of yarn are hung on rods having pinions on their ends, as in the third modification, but the rods and pinions are carried by longitudinal frames which have vertical bars fixed to them, and fitted to work in vertical guides fixed to the side of the tank. The frames carrying the rods are raised and lowered by two revolving shafts, having each two cranks, connecting rods from which are jointed to blocks fitted in guides fixed to the frames. When the frames descend they come to rest on stops before the cranks reach their lowest positions, and remain stationary whilst the cranks move through the lower

parts of their circuits, the blocks then moving down and up again in their guides. The descent of the frames causes the yarn hanks to be lowered or dipped into the dye or other liquid, and the hanks remain so for a short time until the frames are again raised. Whilst the frames are lifted up with the hanks entirely or for the most part out of the liquid the rods carrying the hanks are turned so as to change the positions of the hanks on them by gearing acting on the pinions. Two of the pinions at the middle of the series are in gear with a spur wheel, carried by the frame, and this spur wheel is acted on at the proper time by a toothed segment carried by a continuously revolving wheel. The toothed segment is so placed that the rods are turned and the hanks moved round only when they are raised, more or less, out of the liquid, and when they are less liable to become entangled. Instead of employing a toothed segment and toothed wheels the motion may be imparted frictionally.

“Another modification of apparatus comprised in this invention is for washing the hanks of yarn, and in it two endless chains are arranged to carry rods or rollers with the hanks on them through a long tank or trough. The two endless chains are at one side of the trough and the rollers or rods are over hung from them, so that the hanks can be put rapidly on and off them over their free ends. Rollers are fitted at regular intervals along the two chains, and wheels or pinions are fixed on the spindles of the rollers between the chains to derive motion from guide grooves or racks on the upper edge of the tank side as they are drawn along. The chains are distended and moved by sprocket wheels on horizontal shafts at the opposite ends of the tank, and the yarn hanks are entered at one end and carried down into and through the washing water to the other end of the tank, where they are raised out of the tank and carried back along the upper or return course of the chains. At the point where each roller is connected to the chains there is also jointed thereto a pendent lever having a rod or roller at its lower end, and on each such lower rod or roller are put the lower parts of the hanks that are on the next preceding upper roller, so

that the hanks are carried through the water in inclined or diagonal positions, the lower parts being drawn in advance. Each pendent lever is formed with a short arm extending upwards from the point of attachment to the chains, and as each pendent lever approaches the entering end of the tank its upper arm encounters a stationary pin which causes the lower end to move forward, and so shorten the distance between the lower roller or rod and the preceding upper roller carrying the same hanks. This facilitates the removal of the washed hanks and the putting on of fresh hanks. The endless chains are moved intermittently, which not only gives time for changing the hanks but also renders the washing action more efficient. The liquid expressing apparatus herein-before described may be modified by substituting for the upper plate a roller to be moved over the lower plate, or to have the lower plate moved under it, this constituting a modification intermediate between those herein-before described and that described in the earlier specification herein-before referred to. In some modifications of the liquid expressing apparatus it will be more convenient to make the lower piece move upwards to give the pressure, instead of the upper piece moving downwards, as herein-before described."

The claims which conclude the complete specification are as follows:—

(1) "The expressing of liquids from yarns by pressing them between plates arranged and worked substantially as herein-before described.

(2) The combination of a plate and a roller, arranged substantially as herein-before described, for expressing liquids from yarns.

(3) The combination of a pair of plates for expressing liquids from yarns with endless chains for placing the yarns between the plates and removing them thence, substantially as herein-before described.

(4) The arrangement of a pair of plates for expressing liquids from yarns, wherein a horizontal movement of one plate is made to admit of the yarns being conveniently laid on the lower plate, substantially as herein-before described.

(5) The combination of apparatus for saturating yarns and expressing liquid therefrom, herein-before described with reference to Figures 3 to 6 of the accompanying drawings.

(6) The combination of apparatus for saturating yarns, wherein, in a nearly semi-cylindrical vessel, a wheel with radial arms fitted for carrying rods which hold the hanks in radial positions is made to rotate with alternate short backward and longer forward movements, substantially as herein-before described.

(7) The imparting to yarn saturating or washing apparatus the alternate short backward and longer forward movements derived from a crank or eccentric pin on a pinion which is made to roll at a uniform rate around a fixed wheel, substantially as herein-before described.

(8) The combination of apparatus for saturating yarns, herein-before described with reference to Figures 7 and 8 of the accompanying drawings.

(9) The combination of apparatus for saturating yarns, herein-before described with reference to Figures 12 to 14 of the accompanying drawings.

(10) The arranging of apparatus for saturating yarns, so as to lower the yarns and hold them in the dyeing or other liquid, and alternately therewith raise them out of the liquid and change their positions by turning the rollers carrying them, substantially in the manner herein-before described.

(11) The arranging or combining together of parts of apparatus for washing yarns, substantially in the manner herein-before described with reference to Figures 10 and 11 of the accompanying drawings."

A.D. 1877, March 2nd.—No. 849.

JOHNSTON, FRANCIS. "Improvements in Dyeing, Bleaching, or Printing of Cotton or other Yarns other than from the Hank or Chain, and in Apparatus for Effecting the same." (*This invention received provisional protection only.*)

"This invention relates to an improved apparatus for a more economical and efficient mode of dyeing, printing, and bleaching of cotton or other yarns preparatory to weaving.

"Instead of dyeing, printing, and bleaching of cotton or

other yarns in the hank or chain the yarns are wound on to a yarn beam or beams, technically called 'warper's beam,' or equivalent or equivalents; the said yarn (or 'warper's') beam or beams, or equivalent or equivalents, are placed on suitable bearers or equivalents; the said yarns are then wound on to another beam or beams, or equivalent or equivalents, at the same time passing over or under or under and over suitable rollers or equivalents placed into a vat or vats, or equivalent or equivalents, containing dyeing, printing, or bleaching liquid, and between squeezing rollers or equivalents placed in the said vat or vats or equivalents, or at any other convenient part of the said vat or vats, or equivalent or equivalents, or at any convenient part of the said apparatus, and each thread of the yarns when dried passes through guides or equivalents, then passing between suitable rollers or equivalents, if necessary, then on to the winding-on or 'warper's' beam or beams, or equivalent or equivalents. Now if a darker shade is required the process is repeated, after which the yarns are ready for sizing or other processes necessary preparatory to weaving; and further, if necessary, I connect an apparatus for regulating the tension of the yarns during the process of dyeing, printing, and bleaching, or any other process necessary before sizing such yarns, which I accomplish by fixing a small friction pulley or equivalent on the end of the axle of the winding-on shaft or at any other convenient part of the winding-on apparatus, and another on the end of the squeezing roller or rollers, or equivalent or equivalents, or placed at any other part or parts of the apparatus driven by the winding-on shaft or equivalent by means of a strap, band, or any other equivalent or equivalents thereof."

A.D. 1877, March 3rd.—No. 854.

TRACY, JOHN HART. "Improvements in Machinery or Apparatus for Plaiting or Folding Fabrics." (*This invention received provisional protection only.*)

"Machines constructed according to this invention are fitted with the following principal working or operating parts for effecting the plaiting or folding of fabrics, viz., a box or hollow table heated, by preference, by gas jets; secondly, a

presser plate, the under surface of which is somewhat rough, for the purpose of serving as a feed appliance, such plate rising and falling on the material passing under it, and on or over the aforesaid box or hollow table; thirdly, a back folding knife, which has a downward, a backward receding, and a forward slanting rising motion; and, fourthly, a front folding knife, which has an oscillating back and forward motion and up and down motion against the back folding knife.

"The material to be folded or plaited passes over the front knife, over the back edge of it, round the front edge of the back knife, and between the presser plate and the box or table, passing off straight from the latter, and not as now usually done in some plaiting machines dropping down through a hole in the table, whereby through the weight of the fabric the just formed pleats are partly opened. The aforesaid operating parts of the machine are worked by suitable cam or eccentric appliances, which I place above the aforesaid operating parts, so that the plaited material can freely pass off in a horizontal direction, being supported to any required distance by a table or plate in continuation of the hot box.

"The width of the plates or folds may be regulated by adjusting the stroke of the presser plate and front knife as required.

"The back knife may be worked by bell-crank levers actuated by cams. The presser plate may be similarly actuated, and from cams on the same shaft. The front knife may be actuated from another cam shaft, which is driven by bevil gearing from the main shaft.

"The action of the operating parts of the machine is as follows:—The back knife goes down on the material, the front knife recedes, rises and then advances, carrying the material against and over the back knife, forming a pleat. The back knife then recedes from under the front knife and rises forward in a slanting direction; the first knife is then made to drop and press the fabric on to the table. The presser plate then rises, thus releasing the fabric beneath it; it then goes forward, and is then pressed down on the pleated

fabric again. The front knife is then withdrawn again, and the presser plate moves back, carrying the pleated fabric with it; this presser plate thus serves as a feed appliance."

A.D. 1877, March 3rd.—No. 859.

WILSON, JOHN, and COCHRANE, WILLIAM. "Improvements in Hot Pressing Textile Fabrics, and in the Machinery or Apparatus Employed therefor."

The following is the provisional specification of the patent; the complete specification refers to two sheets of drawings accompanying; it is published at 6d.

"This invention, which relates to improvements in hot pressing textile fabrics, has for its object to render hot pressing a continuous operation, and to diminish the labour and time at present occupied in hot pressing by stationary hydraulic presses.

"The machinery constituting the invention consists of a framing in which is carried the cylinder or drum, by the aid of which and the other parts herein-after described the hot pressing is effected.

"The cylinder or drum is rotated by means of a spur wheel at one end driven by a spur pinion actuated by a belt or otherwise, and the cylinder or drum is heated either by a stationary fire, but preferably by the burning of a mixture of air and gas within it, or it may be otherwise heated with or by a blast of heated air. The framing is provided with any required number of hydraulic cylinders, by preference four, which are placed therein equidistant and vertically to the axis of the cylinder or drum.

"The plunger or ram in each cylinder act upon a slide carried in the framing and so shaped as to hold several small rollers which, by the action of the hydraulic rams, are forced with any required degree of pressure against the cylinder or drum. In this manner pressure is produced round the whole surface of the cylinder or drum, and as the hydraulic cylinders are opposite one another and of equal bore the pressure is balanced at all points. Two webs of paper are passed in between the cylinder or drum and the small pressure rollers which surround it. These may either be in the form of

endless belts or of sufficient length to correspond without break to the length of fabric to be hot pressed. The fabric to be hot pressed is passed in between the webs of paper and continuously carried through the machine with them until sufficiently hot pressed.

"Under a modified form of the machine, the main cylinder or drum may be dispensed with and a succession of heated rollers pressed together, arranged either horizontally or otherwise substituted. Through these sets of rollers the webs of paper and cloth to be finished are led."

The claims of the patentees as set forth in the complete specification are as follows:

"First. Of a large central roller or cylinder surrounded with smaller rollers or cylinders.

"Or, Second. Of a pair or series of pairs of parallel sets of rollers or cylinders, the rollers in each case being heated and forced together with the degree of pressure requisite for the hot pressing or finishing operations, and between which rollers the cloth to be hot pressed or finished is continuously passed, being laid within two endless sheets of pressing paper or their equivalent, substantially as herein-before described and shewn upon the two accompanying sheets of drawings."

A.D. 1877, March 10th.—No. 964.

BYERS, ARCHIBALD STEWART. "Improvements in Scouring, Bleaching, and Dyeing Yarns, and in the Machinery or Apparatus employed therefor." (*This invention received provisional protection only.*)

"This invention has reference to the scouring or washing, bleaching, and dyeing of woollen, cotton, linen, or other yarns or threads in hanks, linked together as a 'chain,' or in long lengths or webs; and to a new or improved general construction or arrangement of machine or mechanism for so doing, in a quicker and better manner, with less strain and wear or fatigue to the fibre or texture, which is of great importance in the said treatment of some of the finer and softer classes of these yarns. And the nature of the invention, or construction of the machine, or arrangement of mechanism and mode of working the same and of treating the yarn therein consist all

as follows :—In this machine, as in others of the same class, the liquid or dye box or cistern is made of strong wood, slate, or metal lined or not, as required, to resist the action of the liquids employed, and made of about the usual size in width and depth (as three feet by four feet respectively), open at the top, and set or fixed on longitudinal scantling or transverse bearers as a sole above the floor.

“By these improvements, however, the yarn guiding and drawing rollers are mounted longitudinally in bush bearings within and above the cistern, having the yarn traversed over them in a series of spiral coils transversely, so that the boxes and rollers do not require to be so long as heretofore (three feet or so being found sufficient) ; but for the convenience of making and to give stability and steadiness when at work they are made duplex, or of sufficient length to make two cisterns, with a division end in the centre of them, each cistern having its own set of rollers driven separately, as a double machine, convenient for putting the yarns through them consecutively to repeat the same treatment, or as a first and second further or different sequential treatment, before removal for finishing by other machines or processes. Three cast-iron or other frames are secured, one to each outer and central dividing end of the cistern, and projecting up from the middle, stayed at the top by a tie bar, and fitted with central bush bearings and slots above for carrying the journals of the shafts of the large main driving or drawing rollers just a little above the top of the cistern, with those of the loose pressing rollers resting and rolling above the main rollers by their own weight, or with weighted levers fitted and resting on their bushes.

“Each of the main rollers is preferably driven separately by a fast and loose pulley mounted on the outer end of its shaft, through an open or cross band or belt passed from a pulley on any adjacent motive-power transmitting shaft or engine ; each being thus quite self-contained, and fitted with a belt-shifting fork lever. Guide rollers are fitted to revolve loosely along near the bottom and two sides of each cistern in bush bearings secured to its inside ends, with a similar roller some little distance higher in the centre between the former, made

movable by its bushes and levers to give any desired stretch to the coils of yarn.

"The long chain of yarn (in warp, or attached together by loose loops of twine when in hanks) is fed in, preferably, at the adjacent ends of each machine through a new or improved frame of undulating tension pins or 'pace' rollers, over and under as many of these pins or rollers as will give the desired stretch or tension to the yarn in passing into and through the machine, from which it passes through a usual porcelain guide eye, also mounted at this end so as to lead the yarn in between the main driving roller and the loose pressing roller above it, down and round the small guide roller at the bottom and off side of the cistern, and up over the lower middle guide roller, down and under the guide roller at the bottom and near side of the cistern, then up over the main driving roller, and again through between it and the pressing roller above; and so on for as many times or coils, spirally, as will suffice for the particular kind of yarn and work in hand (from eight to twelve times, answering for the size of machine described), each turn or coil being kept separate by a longitudinal bar fixed below one or both sides of the main roller, with a regular divided line of separating pins or rollers projecting out through the line or plane of the yarn. In passing between the lower side rollers and main roller, the yarn is finally lead off over the upper outer end of the top roller, through, below a small india-rubber covered pressing roller, carried on loose lever arms oscillating on the upper stay, or sliding without levers in guides on the end frame or other equivalent, to slightly press the liquid out of the yarn before leaving the machine through its leading-off porcelain eye mounted at that end, assisted by a small drawing-off winch. Each cistern is fitted with the usual inlet and discharge liquid taps and pipes, or couplings and hose; and also with heating rose steam pipe along the bottom inside, with controlling tap or valve outside.

"For carrying the chain of hanks of yarn from the delivery end of one machine and cistern to the inlet end of the other, when this is desired, an endless travelling web of strong blanket cloth or other equivalent is mounted on two end and

intermediate guide rollers, carried in a portable rectangular, inclined, or horizontal frame set or fitted on the floor at the side of the machine, where it will receive the yarn from the delivery end or winch of the first machine loosely on the top of its back or lower end, and convey or carry it to the other or upper end, where it will be fed in through the improved tension frame of undulating pins or rollers and inlet porcelain eye; then round the rollers and through the cistern of the second machine, all otherwise in an undulating or spiral coil, substantially as described in reference to the first machine, and from which it is led off at the outer end into removing vessels, to be further treated or finished.

“The endless carrying web or blanket is driven by a belt or band passed over a pulley on the end of one of its driving rollers, from a pulley on one of the spindles of the main rollers, or on an axis driven by it; and while the chain of hanks is being traversed over the top of this travelling web, the attendants get time to shift or turn the hanks or their twine or other cord attachment to a fresh place, when this is considered necessary or advisable to prevent injurious markings across the hanks.”

A. D. 1877, March 13th.—No. 1005.

SUMNER, WILLIAM. “Improvements in Apparatus for Drying Yarn, Woven Fabrics, and other Materials.” (*A communication from Tulpin Brothers, of Rouen.*)

“This improved apparatus may be used for drying warp yarns after they have been sized in the ordinary sizing machine; or for drying woven fabrics or paper, or any other substance or material, and it consists of any convenient number of steam chests placed either horizontally, vertically, or diagonally, between which the yarn or other material is caused to travel slowly, being guided over rollers placed near the ends of the chests, the spaces between the chests forming any number of compartments, according to the nature of the material to be dried and the degree of drying required.

“The chests are all supplied with steam from a main pipe, and another pipe is provided to carry off the water of condensation; a safety valve is also applied to the supply

pipe. A current of air is forced or drawn through the spaces between the steam chests to evaporate and carry off the moisture, and this current of air is produced by a fan, or by a steam jet or other equivalent means."

The above is the provisional specification; the complete specification has one sheet of drawings and is published at 6d. The claim is worded as follows:—

"The improved drying apparatus described, consisting of any convenient number of steam chests surrounded by a box, through which currents of air are forced or drawn by a fan or other equivalent."

A.D. 1877, March 14th.—No. 1015.

JAMIESON, EDWARD, and COLLINS, HENRY. "Improvements in and Apparatus for Shrinking Textile Fabrics."

"The object of this invention is the more effectual shrinking of woollen, cotton, linen, and other textile fabrics, whereby the same shall be less liable to shrink after being made up into garments than when treated in the ordinary manner.

"Now this invention consists in submitting such fabrics in the piece to the action of steam in such a manner that the whole length of the piece shall be equally acted upon by the steam, for which purpose we arrange an enclosed chamber with a series of parallel laths or rods at the upper part, and over and between which laths or rods the fabric is suspended loosely, so that when steam is admitted to such chamber, either from any convenient steam supply or from a boiler placed within the steam chamber, and heated by gas or otherwise, the steam finds ready and equal access to all parts of the piece.

"It will thus be apparent that in accordance with this invention the whole piece, being suspended loosely in the steam chamber, is free to shrink to any desired extent under the direct action of the steam.

"Upon removing such fabric from the steam chamber we at once roll it together whilst in its heated state, and thus permit it to dry itself, after which it will be found to be permanently and effectually shrunk."

The above is the provisional specification, the complete

specification is illustrated by a sheet of drawings, and is published at 6d. The claims are—

“ 1st. The method of shrinking textile fabrics in the piece, as herein-before described and illustrated in the accompanying drawing.

“ 2nd. The general construction, combination, and arrangement of apparatus for shrinking textile fabrics in the piece, as herein-before described and illustrated on the accompanying drawing.”

A.D. 1877, March 16th.—No. 1056.

JACKSON, WILLIAM, of Urmston, near Manchester. “Improvements in treating Fabrics Printed with Aniline Colours.”

“When fabrics have been printed with certain aniline colours, and particularly with aniline blacks, it frequently if not always happens that the colours fade after a few days' exposure to the atmosphere. Now, my invention consists in so treating fabrics printed with aniline colours, that the colours shall be made fast on the fabrics, and that colours that have been allowed to fade by exposure shall, to a great extent, be restored.

“In performing my invention immediately, or soon after the fabrics have been printed with the aniline colours in the ordinary manner, they are passed through a solution of carbonate of soda, or the ordinary soda of commerce, combined with chloride of sodium, or the common salt of commerce, in the proportion of six ounces of soda and one ounce of salt to one gallon of water, the fabrics are then dried, and the aniline colours are by this means effectually fastened on the fabrics.

“When fabrics printed with aniline colours have been allowed to fade by exposure to the atmosphere, they may be restored by passing the printed fabrics through a solution of the above description.

“My invention may be modified by mixing the soda and salt with the starch or other ingredients employed for finishing the fabrics printed with aniline colours; or the fabrics may be printed and finished in the ordinary manner, and then passed through the solution above described to fasten or restore the aniline colours.

"Having thus stated the nature of my invention and described the manner of carrying the same into practical operation, I wish it to be understood that I do not intend to limit myself to the details or proportions given, and I claim the improved mode of treating fabrics printed with aniline colours, whereby the colours are fastened or restored, as described."

A.D. 1877, March 16th.—No. 1066.

SMITH, SAMUEL MILNE, SMITH, CHARLES TELFORD, and BINNS, WILLIAM. "Improvements in Finishing 'Moreens' and Corded Fabrics."

"This invention relates to a method of finishing corded fabrics in such manner that a definite pattern or design may be produced on the watered surface, in addition to the ordinary or indefinite watered pattern always produced, by pressure upon two corded fabrics placed face to face.

"Our improvements consist in having a raised pattern woven upon one piece and pressing the woven piece and an ordinary plain piece together, face to face in the usual manner, the result being that both of the pieces bear a distinct and similar impression of the pattern in addition to the ordinary watered impression.

"Having now described the nature and particulars of this our invention, and the manner in which the same is to be put into practice, we would have it understood that what we consider to be new, and therefore claim as our invention, is the employment in the process of finishing fabrics of two pieces, one being plain and the other having a raised woven pattern, as and for the purpose herein described."

A.D. 1877, March 19th.—No. 1096.

WOODCOCK, EXLEY, and WOODCOCK, JOHN WILLIAM. "Improvements in 'Hawking Machines' for Indigo Dyeing."

"This invention has reference to a patent granted to Oldroyd, Woodcock, and Coulter, No. 3223, A.D. 1870. In the specification of this patent mention is made of bands, cords, or tapes passing through grates and over and around rollers for the purpose of guiding the fabric into the liquor and preventing such fabric adhering to and passing around

the nipping or squeezing rollers, the tendency of the fabric being to do so. In practice it is found that these bands, cords, or tapes are objectionable, not only in consequence of the frequent breakages of the cords, which require replacing, but more especially as regards the marks or impressions they leave on the piece or fabric; when dyed the fabric is also cut or "chaved." Now, our invention is intended to dispense with these bands, cords, or tapes, and remove these defects; and the improvements consist in the use or employment of one or more rollers revolving in the same direction as the squeezing rollers, and in close proximity thereto; also of a scraper or other suitable instrument working in contact with the additional rollers, so that the fabric is guided into the liquor and effectually prevented lapping round the squeezing rollers. The squeezing rollers are brought together by springs, and we so arrange the additional rollers and scraper that they are supported by and attached to the same framework which supports the springs and squeezing rollers; therefore when an uneven part of the fabric is passing through the rollers the springs allow of their being pushed apart, the additional rollers and scrapers also being moved away, so that they all maintain the same relative position to each other; or instead of using another roller we may apply the scrapers direct to the squeezing rollers."

The above is the provisional specification; the complete specification is accompanied by one sheet of drawings and is published price 6d. Claim is for the roller and scraper.

6. *British and Foreign Patents, from the Commissioners of Patents Journal, October 2nd to October 26th, 1877, inclusive.*

Production of Colouring matters.

2602. WILLIAM ROBERT LAKE, of the firm of Haseltine, Lake, and Co., Patent Agents, Southampton Buildings, London, has given notice to proceed in respect of the invention of "An improved

- manufacture of red colour."—A communication to him from abroad by Johann Zeltner, of Nuremberg, Bavaria.
3438. WILLIAM FORD STANLEY, of Great Turnstile, Holborn, London, for the invention of "Improvements in colours."—Provisional protection has been granted.
3698. JOHN PETER GRIESS, of Burton-on-Trent, Chemist, for an invention of "Improvements in obtaining colouring matters suitable for dyeing and printing."—Dated 4th October, 1877.—Notice to proceed has been given.
2614. WILLIAM ROBERT LAKE, of the firm of Haseltine, Lake, and Co., Patent Agents, Southampton Buildings, London, has given notice to proceed in respect of the invention of "Improvements in the manufacture of violet colour."—A communication to him from abroad by Johann Zeltner, of Nuremberg, Bavaria.
3731. HEINRICH CARO, Chemist to the Badische Aniline and Soda Works, of Mannheim, in the empire of Germany, for an invention of "Improvements in the production of coloring matters suitable for dyeing and printing."—Dated 8th October, 1877.—Provisional protection has been granted.
3737. REINHOLD HOFFMANN, of Marienberg-bei-Bensheim, in the empire of Germany, Chemist, for an invention of "Improvements in the production of colouring matters."—Dated 9th October, 1877.—Provisional protection has been granted.
3751. HEINRICH CARO, Chemist to the Badische Aniline and Soda Works, of Mannheim, in the empire of Germany, for an invention of "Improvements in the production of colouring matters suitable for dyeing and printing."—Dated 9th October, 1877.—Provisional protection has been granted.

**Dyeing and Printing Colours, Mordanting, Preparing,
Singeing, Bleaching.**

1648. GEORGE CANTRELL GIBBS, of Brentford, in the county of Middlesex, for an invention of "Improvements in machinery or apparatus for dyeing and colouring felt, silk, and other textile or porous fabrics."—Dated 27th April, 1877.—Sealed October 20th, 1877.
2197. HENRY DEWHURST, of Huddersfield, in the county of York, Woollen Printer, has given notice to proceed in respect of the invention of "Improvements in mordanting or preparing woven or felted fabrics for printing."

3617. JOHN IMRAY, of 20, Southampton Buildings, in the county of Middlesex, for the invention of "Improvements in the bleaching and cleansing of textile vegetable materials."—A communication to him from abroad by Paul Bayle, Merchant, and Rinaldo Pontiggia, Chemist, both of Paris, France.—Provisional protection has been granted.
3742. THOMAS HOLLIDAY, of the firm of Read, Holliday, and Sons, of Huddersfield, in the county of York, Manufacturing Chemists, for an invention of "Improvements in dyeing textile fabrics black or grey colours with aniline."—A communication to him from abroad by William Jules Samuel Grawitz, of 1, Boulevard Henry IV., Paris, in the republic of France.—Dated 9th October, 1877.—Provisional protection has been granted.
2692. JOHN LIGHTFOOT, of Lowerhouse, near Burnley, in the county of Lancaster, Chemist, for an invention of "Improvements in printing and dyeing textile fabrics and yarns."—Dated 12th October, 1870.—The £100 stamp duty has been paid.
2787. JAMES WORRALL, of Manchester, in the county of Lancaster, Dyer, for an invention of "Improved apparatus for singeing fabrics."—Dated 22nd October, 1870.—The £100 stamp duty has been paid.
3632. ALEXANDER MELVILLE CLARK, of 53, Chancery Lane, in the county of Middlesex, Patent Agent, for an invention of "Improvements in dyeing threads, yarns, and fabrics aniline black."—A communication to him from abroad by William Jules Samuel Grawitz, of Paris, France.—Dated 21st October, 1874.—The £50 stamp duty has been paid.
- 43,208. A. F. ARMAND, of Morlanwelz-Mons, for "A machine for heating, boiling, bucking, and washing linen, &c."—Dated 29th September, 1876.—Belgian patent.
- 116,602. KINSBOURG and ROBERT, sen., of Paris, for "Obtaining so-called 'indestructible aniline blue' by the previous sizing of cotton or other vegetable substances for black aniline dyes."—Dated 22nd January, 1877.—French patent.
101. C. D. BROCHOCKI and Co., of Paris, for "A decolouring agent called 'Eau de javelle.'"—1 year.—Dated 11th June, 1877.

Yarn and Wool Treatments.

2208. ANDRE' PROSPER ROCHETTE, of Petit-Quevilly, près Rouen, in the republic of France, has given notice to proceed in respect

of the invention of "Improvements in washing wool, and in solutions employed for this purpose."

3427. JOHN COLLINS, of Glasgow, in the county of Lanark, North Britain, Engineer, for the invention of "Improvements in machinery or apparatus for washing, scouring, and dyeing yarns."—Provisional protection has been granted.
3603. JOHN CRAWFORD MUNN, of the firm of Munn and Hughes, of the city of Glasgow, in the county of Lanark, North Britain, for an invention of "Improvements in dyeing yarns for warps."—Dated 20th October, 1874.—This patent has become void.
2772. JOHN McNAUGHT and WILLIAM McNAUGHT, junior, both of St. George's Foundry, Rochdale, in the county of Lancaster, Engineers, for an invention of "Improvements in machinery or apparatus for washing, opening, and drying wool and other fibrous materials, and washing yarns."—Dated 21st October, 1870.—The £100 stamp duty has been paid.

Finishing Operations, Enlarging, Plaiting, Tenterring, Folding, Mangling, Stretching, Spreading, Beetling, etc.

1386. FERNAND DEHAÏTRE, of the firm Pierron et Dehaitre, of Boulevard Saint Denis, 1, at Paris, Mechanics, for an invention of "An improved machinery or apparatus for enlarging fabrics of all kinds."—Dated 9th April, 1877.—Sealed.
1476. NEWTON WILSON, of High Holborn, in the county of Middlesex, Sewing Machine Manufacturer, for an invention of "Improvements in machinery or apparatus for plaiting fabrics."—Dated 16th April, 1877.—Sealed October 13th, 1877.
2134. WILLIAM ROBERT LAKE, of the firm of Haseltine, Lake, and Co., Patent Agents, Southampton Buildings, London, has given notice to proceed in respect of the invention of "An improved cloth-stretching or tenterring machine."—A communication to him from abroad by Claude Garnier, of Lyons, France, Cloth Dresser.
2261. FERDINAND RATH, of Goldsmith Street, in the city of London, has given notice to proceed in respect of the invention of "Improvements in machinery or apparatus for plaiting or folding woven or other fabrics."
3419. JOHN FISHER, Manager of the Dundee Calendering Company, Dundee, in the county of Forfar, North Britain, has given

notice to proceed in respect of the invention of "Improvements in mangling, calendering, or finishing linen, and other fabrics."

3451. BARKLEY CHARLES WILSON, of the firm of Wilson, Collett, and Company, of the city of London, Lace manufacturers, for the invention of "Improvements in machinery or apparatus for plaiting fabrics."—Provisional protection has been granted.
3628. WILLIAM EDWARD NEWTON, of the office for Patents, 66, Chancery Lane, in the county of Middlesex, Civil Engineer, for the invention of "Improvements in machinery or apparatus for stretching fabrics."—A communication to him from abroad by Alfred Francois Lacassaigne, of Paris, in the republic of France.—Provisional protection has been granted.
2610. WILLIAM BIRCH, of Salford, in the county of Lancaster, Machine Maker, for an invention of "Improved self-acting machinery for opening, smoothing, spreading, and guiding calico, cloth, and other fabrics for the use of bleachers, dyers, calico printers, and others."—Dated 1st October, 1870.—The £100 stamp duty has been paid.
3430. FOSTER CONNOR, of Belfast, in the county of Antrim, in Ireland, for an invention of "Improvements in machinery for beetling fabrics, yarns, and fibrous substances."—Dated 7th October, 1874.—The £50 stamp duty has been paid.
32. P. MAGNER, of London, for "Improvements in the treatment of vegetable fibres for giving them a silky appearance and preparing them for dyeing."—3 years.—Dated 3rd March, 1877.—Bavarian patent.
- 190,786. JAS. SHORT, of East New Brunswick, N.J., for "Finishing woven fabrics."—Application filed 17th October, 1876.—United States patent.
- 190,548. C. C. BUTTERWORTH, of Philadelphia, Pa., assignor to himself and J. Butterworth, of the same place, for "Drying-cylinders."—Application filed 7th April, 1877.—United States patent.

THE TEXTILE COLOURIST.

No. 24.]

DECEMBER, 1877.

[Vol. IV.

*1. Note upon the Adulteration of Ground Madder and Preparations of Madder, such as Flowers of Madder and Garancine.**

BY M. CH. BENNER.

THE adulteration of madder by mixing it with some inert powder or other incorporated with an extract of dyewood or powerful astringent has been practised from time immemorial.

The spent tan of the leather works properly dried and ground is particularly well adapted for this kind of fraud. According to circumstances there is added to it extract of chestnut, dry extract of pine bark, peachwood, or logwood, and sometimes in particular cases, a mixture of the three extracts in varying proportions are added to the spent tan.

These frauds were extensively practised about the years 1858 to 1862, and were principally used to increase the strength of certain qualities of madder and garancines which were for exportation.

The Avignon Chamber of Commerce was annoyed at the existence of this state of things, and in 1859 it offered a prize of 10,000 francs for the discovery of an easy and rapid method of detecting the adulteration of madder and the products made from it.

From the competition for the prize there was one process,

* Read at the Industrial Society, Rouen, August 3rd, 1877, from the Bulletin of the Society, v., 446.

that up to a certain point answered the end sought, though it did not gain the prize. This process consisted in the use of white blotting or filtering paper, which being cut into slips, was dipped into a solution of bichloride of tin at 2° B., drained, and then placed upon a piece of glass. Another slip of paper was steeped in a solution of sulphate of iron, drained, and then placed side by side with the other dipped in the bichloride of tin. A portion of the paper while still moist is dusted with the powders to be tested; to do this evenly a pencil is employed, with which the powder is taken up and shaken off again. Upon another portion of the paper a sample of the same merchandise known to be quite free from adulteration is applied in like manner, and upon a third portion is dusted some powder which the operator has himself prepared, and containing known quantities of the different adulterants likely to have been employed; by thus operating it is possible to judge by a single trial of the purity or the greater or less degree of the adulteration.

The action is allowed to go on for fifteen or twenty minutes. At the end of this time the under part of the glass plate is gently heated until the paper is quite dry. The powders are now shaken off the papers, and the different coloured stains produced by contact of the materials are noted.

Pure madder, flowers of madder, or garancine do not give any suspicious stains to these test papers; but if there has been any, even a very small addition of any extracts, dye-wood, or astringent matter, one or other of the papers will shew the adulteration, and from the number and extent of the coloured stains the amount of adulteration can be roughly estimated.

One adulterant, however, is difficult to detect by this process, it is the green tannin from the bark of resinous woods, such as that of the pine. It can be made evident in part by moistening the test paper with alcohol after it has been dried, and allowing it to dry again spontaneously. It will be detected by the sulphate of iron paper.

Since the period above referred to a better system of testing was worked out by three members of the Society of

Emulsion in Rouen, and was described in the Bulletins of this Society for the years 1863-64.

Five grammes of the sample to be tested are weighed out, and 65 grammes of warm distilled water added, and afterwards 35 grammes of commercial alcohol; the mixture is stirred and left for fifteen minutes, then filtered, the filtered liquid being received in a porcelain dish. In this liquid slips of bibulous paper are dipped, so as to be impregnated as uniformly as possible with the liquid, and then they are dried in the air. It is upon these carefully dried papers that the tests are made with solutions of the following salts.

In making these experiments there will naturally be taken for comparison a sample of a pure colouring matter, which enables the observer to judge more certainly of the difference of the reactions which may take place:—

(1) Acetate of copper made by mixing 10 grammes sulphate of copper, 10 grammes acetate of lead, and 100 grammes distilled water.

(2) Acid chloride of tin prepared with 20 grammes protochloride of tin, 5 grammes hydrochloric acid, and 100 grammes of distilled water.

(3) Nitrate of silver, a ten per cent. solution.

(4) Protosulphate of iron, a ten per cent. solution.

(5) Carbonate of soda, a ten per cent. solution.

The reagent is applied to the paper by a pencil prepared by making a small roll of a bit of white calico. A couple of marks are made upon the paper steeped in the solution, and they are left to dry during three-quarters of an hour in the shade.

At the end of this time the papers are compared and the purity of the samples estimated, which is easy to do from the differences observable between the effects produced upon the papers from adulterated and pure qualities.

In order to more certainly detect the green tannin matters which may have been added to a madder derivative, and to operate upon solutions not so much coloured with the natural brown colouring matters of madder, the infusion may be subjected to fermentation; a process which does interfere

with the success of the trial. For this purpose 100 grammes of the madder to be tried are mixed with 375 grammes of water at 100° F. and 5 grammes of beer yeast, and the mixture left for a night in a warm place; in the morning, 500 grammes of water at 120° F. and 200 grammes of alcohol are added and left to digest for half an hour, the liquid filtered, and the white bibulous paper soaked in the solution, which after being dried is treated with the reagents as above.

This second method acts perfectly well as a control upon the simpler process.

A third manner of testing the purity of these matters is as follows:—A slip of the bibulous paper is suspended by a pin to a cross support, and the end allowed to dip in the liquor which has been used to wet the previous test slips, and left in that position all night. The capillary attraction of the unsized paper causes the liquor to be drawn up, and the oxidation effected by the air causes the paper to assume a special colour, according to the nature of the foreign substance which has been added to the garancine; in this way by repeating the trials once or twice the appearance of the paper will give the information sought, which may be confirmed in an indisputable manner by the reagents.

Inert matters which may have been added are estimated by the quantitative dyeing test in the usual way.

As a supplement to this paper of M. Benner's, we may transcribe from the same journal an account of a curious collection of adulterated samples of garancine which was exhibited recently at the Horticultural Exhibition at Amsterdam. These were nearly all contributed by M. Benner, and are described by M. Dépierre, along with a large and interesting collection of madder products, of which an account is given further on. This series contains the following examples:—

No. 1.	Garancine adulterated with 10 per cent.	mahogany wood.
” 2.	”	” 9 ” saw-dust.
” 3.	”	” 10 ” Brazil wood.
” 4.	”	” 50 ” spent garancine.

- No. 5. Garancine adulterated with 12 per cent. cocoa husks.
- | | | | | | | |
|-------|---|---|---|----|---|-------------------|
| " 6. | " | " | " | 10 | " | yellow ochre. |
| " 7. | " | " | " | 10 | " | sandal wood. |
| " 8. | " | " | " | 10 | " | bran. |
| " 9. | " | " | " | 10 | " | logwood. |
| " 10. | " | " | " | 10 | " | red ochre. |
| " 11. | " | " | " | 10 | " | ground brick. |
| " 12. | " | " | " | 10 | " | sapan wood. |
| " 13. | " | " | " | 10 | " | yellow sand. |
| " 14. | " | " | " | 8 | " | almond shells. |
| " 15. | " | " | " | 12 | " | yellow clay. |
| " 16. | " | " | " | 1 | " | logwood extract. |
| " 18. | " | " | " | 10 | " | dry pine extract. |
| " 21. | " | " | " | 8 | " | chestnut extract. |
| " 22. | " | " | " | 50 | " | dyeing residues. |
| " 25. | " | " | " | 10 | " | elm bark. |
| " 26. | " | " | " | 10 | " | of spent tan cal- |

cined with addition of 50 per cent. of sour tan from the pit.

" 27. Sample of spent madder dried and pressed for purposes of adulteration.

" 28. Compound powder for adulterating garancine. This powder contained—

100 parts spent tan,
 5 " extract of logwood,
 1 " " of peachwood,
 5 " " of chestnut.

There were also samples of various other substances used for the purposes of sophistication. The dates of the samples in this collection range from 1840 to 1863.

2. *Collection of Samples of Madder and its Products at Amsterdam.*

M. J. DEPIERRE has given an interesting account of a large collection of madder samples which was got together by

some members of the Industrial Society of Rouen, and exhibited at the Horticultural Exhibition at Amsterdam this year. He gives a complete catalogue of them to the number of two hundred and thirty-four samples. We abstract some points of general interest from his report. In an album containing about thirty specimens of dried madder plants there were a number collected by the celebrated Linnaeus, and endorsed by him with the name in French written "Garence." The collection of garancine dates from 1840, commencing with a sample of Lagier's make, one of the earliest manufacturers, and including numerous authentic specimens of all the best-known makes down to 1876. All known varieties of madder and flowers of madder, with some other products of historical interest, were to be found in this exhibit. We may enumerate a sample of colorine of Girardin and Grelley, dating 1840, which was probably the first extract of madder ever used for printing; an essence of madder, dated 1853, having fifty times the dyeing power of madder; Kopp's purpurine and green and yellow alizarine, dated 1859; a great variety of extracts of madder; and a collection of various coloured madder lakes, of the manufacture of Courtois and Co.; crystallized and amorphous alizarine; and among the rarer madder products may be mentioned rubian, xanthopurpurine, oxyalizarine, hydrate of purpurine, Rosenstiehl's pseudo-purpurine, oxalic acid from madder, madder alcohol, madder gum, madder sugar, and madder camphor, as well as pectic acid from madder. The collection of adulterated garancines has been mentioned in the preceding article.

The whole collection (excepting the album) is, we understand, to remain permanently in the Museum of Products belonging to the Industrial Society of Rouen. The commission of the Amsterdam Exhibition thought so highly of this collection as to award to it their highest recompense—the large gold medal. When we read of this and similar efforts made by the Society of Rouen and its elder sister the Society of Mulhouse, in connection with the trades which have conferred prosperity upon those towns, we cannot help a feeling of regret, and indeed something approaching to shame,

that Manchester, which is a far more important centre of the same industries, should have no such society and no such collections.

3. *Note upon the Future of Madder.**

BY M. J. DÉPIERRE.

IF there is an agricultural product which more than another deserves the attention of not only the cultivator, but also the scientific man and the manufacturer, it is certainly madder.

The growth of the plant employs immense tracts of land, and its applications as a colouring matter are the basis of a large trade. Very few substances have given occasion to such numerous and remarkable investigations, but apart from its scientific bearings, it is very important to enquire whether the plant, which has been so eminently valuable, is destined to disappear from cultivation, or whether by the adoption of new methods or improvements it may yet be able to struggle against its newly-born and powerful rival, artificial alizarine.

It may be asked at the outset whether it is possible to obtain from alizarine the colours with which the manufacturer has hitherto been furnished by madder, garancine, and other like products.

At the present time the answer is in the negative; for though reds, pinks, lilacs, etc., can be, and are now produced, some other colours, such as the shades of chocolate (*puce, maroon, grenat*), have not been worked, although it is known that with a mixture of purpurine and alizarine the latter colours can be easily obtained, but purpurine is not yet a commercial article, notwithstanding many attempts to manufacture it. The problem of its production may, however, be considered as solved, and within no very distant period purpurine will be an article of consumption.

* Bull. de la Soc. Ind. de Rouen, v., 442. Read August 3rd, 1877.

It is not necessary to speak of the fastness of alizarine colours, for practical men know that they are very fast, and in some cases superior to madder colours. There is no question now about the high value of the colouring matter, for in addition to numerous improvements in its manufacture, the methods of its application upon cloth have been perfected, and its employment continues to spread.

The importance of the manufacture of artificial colouring matters is shewn by the following figures, which are for the production in 1875 :—

Germany produced value of.....	30,500,000	francs.
England " " 	9,000,000	"
France " " 	7,000,000	"
Switzerland " " 	7,000,000	"

making a total of fifty-three millions. In 1862, some years before artificial alizarine was known, the total value of the artificial colouring matters produced was twelve millions; a great part of the difference is due to anthracene and artificial alizarine. Thus in 1875 Germany alone produced artificial alizarine to the value of fifteen millions of francs. There are fifteen manufactories—twelve in Germany, two in Switzerland, one in England, and one in France—the whole daily production of which may be estimated at 3,500 kilogrammes, an annual turn out of about 1,000 to 1,100 tons. This production will no doubt be further augmented, especially if, as it is probable, artificial alizarine should entirely supplant madder.

The production of madder in Europe may be estimated at about 48,000,000 kilogrammes, which containing say 1 per cent. of alizarine, is equal to about 480 tons of the colouring principle.

Of this quantity France grows from 20,000,000 to 25,000,000 kilogrammes. To replace the whole quantity it would require an annual production of 4,800,000 kilogrammes of artificial alizarine paste containing 10 per cent. of dry matter. Supposing that anthracene yields as an average 50 per cent. of its weight of dry alizarine, the annual requirements of this article would amount to about 1,000 tons; this quantity correspond-

ing to the distillation of more than 1,000,000 tons of coal. The manufacture of coal gas in France alone consumes nearly 700,000 tons, and in England nearly 2,000,000 tons. There consequently exists the means of furnishing the raw material for a considerable extension of the manufacture.

In 1876, Germany alone supplied nearly 4,000,000 kilogrammes of 10 per cent. alizarine paste, and each year shews a considerable increase.

Within the last three or four years, considerable quantities of madder were used for the preparation of extracts, but at the present time these products have suffered a considerable reduction in value from the competition of artificial alizarine and diminished consumption; thus, in another way decreasing the demand for the primary material.

Can anything be done to change this situation? Can it be expected that artificial alizarine will decline from its position in course of time? To the last question a negative response may be made, for alizarine has established itself firmly in manufactures, and if madder growers do not make vigorous efforts the struggle will end in their discomfiture.

At the present date (May, 1877) alizarine of 10 per cent. costs on an average 5 francs the kilogramme. For madder to compete with alizarine it is necessary that garancine should be sold at a price not exceeding 1 franc 60 cents the kilogramme; to make garancine at this price, Palud's madder should not cost more than 30 to 35 francs the 100 kilogrammes.

Our colleague, M. Leenhardt, member of the Chamber of Commerce of Avignon, reports from an investigation made in 1875, that if Palud madder could be sold at about 50 francs the 100 kilogrammes, the grower could still make its cultivation remunerative; but we have seen that to compete successfully with the artificial product it must be sold at about 30 francs the 100 kilogrammes, and in this difference lies the whole question.

We will only briefly point out what are the conditions under which competition is possible. To those who are interested in this serious question we would recommend the

study of M. Leenhardt's remarks upon it, and we may say with him that there is no chance of a successful struggle except under the following conditions :—

(1) Selection of seeds and choice of soil. It is known that some soil is more suited than others to the growth of madder, other conditions of care and costs being equal.

(2) The prudent use of manure and the more extended application of fertilising agents.

(3) Better methods of converting the madder into garancine and other products.

(4) Utilizing more completely the residues of the washing waters, etc.

(5) More rapid processes of manufacture. By the present methods there is considerable loss which could be avoided.

(6) Immediate grinding of the roots. The roots generally deteriorate by storing, while the powder of the same roots increase in value.

(7) Lastly, an intelligent application of mechanical and chemical aids which are available.

By these means alone can the future prospects of madder be saved from great danger, but it will always require constant and earnest efforts to enable the natural product to struggle without disadvantage against the artificial one.

4. *Note on the Steaming Apparatus of M. D. Sifferlen.*

IN the Bulletin of the Industrial Society of Mulhouse for November, 1877, M. Sifferlen, manager of an important print-works in Moscow, describes some modifications introduced by him into steaming arrangements. These improvements date from 1872, in which year the author deposited a sealed description of them, illustrated by drawings, in the archives of the Mulhouse Society. He has recently asked that this description should be opened, and submitted to the examination of the proper sections. This has been done, and all the

documents and drawings published along with a report by M. Prud'homme.

The first is a letter from M. Sifferlen to the President of the Society, in which he states the utility of his improvements as follows:—

(1) The dispensing with greys and other accessories used in the ordinary methods of steaming by suspending the pieces, fold by fold, from separated points, so as to leave a space between each fold.

(2) To prevent condensation of steam upon the metal in contact with the pieces, I heat the hook or point carriers by a tube through which steam is passed.

(3) Stains by drops of water from the upper part of the steaming box are prevented by a double cover heated by steam.

(4) Lastly, to avoid the loss of time in unhooking the steamed goods, I have invented an arrangement by which the whole of the pieces are unhooked instantaneously.

The next document is an explanation of the arrangement, referring to the drawings, which may be condensed as follows:—The roof of the steaming box is flat, and essentially a steam chest, through which a small current of steam is kept passing. The steam is introduced into the box itself by a large pipe at the bottom bored with holes, above which is a wooden floor perforated in all directions. To secure an equal distribution of the steam, each side of the box is provided with three openings, which are connected by pipes leading into one blow-off pipe. This appeared necessary to obtain a regular displacement of the steam and an equable amount of steaming; the pieces not changing their position, as in the ordinary arrangements during the steaming, rendered this precaution more important.

A carriage bears a frame or square formed by two iron pipes, tinned on the outsides, and joined by two iron cross-bars. Upon these pipes are the rings carrying the points or hooks, of which there are about four hundred upon each pipe. At one of the extremities a lever is placed, which is part of the unhooking arrangements.

The hooking-on is done in the same way as in the arrangement known, in making up, as the rectometer, with this difference, that two boys bring up the rings and arrange the folds as a third workman hooks on the cloth. For 1,000 metres of cloth this operation requires thirty-five to forty minutes.

The hooking being finished, the four sides are covered with wrapping, which is fixed to the points by a brush; then above and below the pieces are covered with cloth stitched on a wooden frame. If the pieces are not completely surrounded they will not be evenly steamed.

To prevent condensation of steam upon the ring points, the tubes which carry them are heated by steam before the wagon is run into the steaming box. This is easily done by connecting them for a few minutes with a steam pipe.

When the pieces are steamed and the wagon run out, the coverings are removed, and then by a movement of the levers which turn the carrying tubes of the ring points partly round inwards the pieces all fall at once to the ground.

While one lot of pieces is being steamed another lot is being prepared on another wagon, so that no time is lost.

The explanation seems complicated, but the result is that double the amount of work can be got through in a day than was possible with the old apparatus.

The third document is a report by M. Prud'homme upon M. Sifferlen's communication, which we reproduce with slight abridgment.

"The steaming apparatus most generally employed at present* consists of a vertical vat, cylindrical or rectangular, in wood, masonry, or metal. The steam is admitted by a sort of watering-pot rose between double bottoms, covered over by a diaphragm of wrapping cloth. These vats are provided with a flat cover, or an angle cover, to lead off the water condensed. The vat is worked from the top; the pieces are not thrown in any way, as that would lead to not

* That is in France, and principally in Alsace. In England such a steaming arrangement could hardly be found.—*Ed.*

only marking off, but to an irregular action of the steam. The most ordinary method consists in rolling them up with a grey piece, so as to prevent chance of marking off. The roll thus obtained is hung on an angular roller fixed on the upper part of the vat, which is connected with a movement outside, by which the roller can be turned round, and change the position of the pieces.

"Occasionally for certain articles the goods to be steamed are hooked upon a spiral frame, such as is used in indigo dyeing, or are suspended vertically in alternate folds to the opposite sides of a rectangular frame. It has been recently proposed to roll the pieces round a cylinder of wire gauze.

"It can be seen at a glance this method of working from the top requires a considerable amount of time and labour. In M. Sifferlen's apparatus the pieces are introduced by a wagon, the entrance is at one of the vertical sides of the box, and consists of a two-leaved door, which is secured in its place by proper means. The general arrangement is not new; it is described in Persoz (Edit. 1846) as having originated in England. The system of suspending the pieces consists in hooking them on rings which slide upon an iron tube and capable of turning with it. To prevent condensation upon the metallic parts of the apparatus they, being hollow, are warmed by passing steam through them before going into the steaming box. The use of greys is unnecessary, it suffices to surround the goods with wrapping. The point upon which the goods are hooked by the selvage is horizontal, and fixed to a vertical piece which is part of the ring. These hooking rings slide, but cannot turn round upon the bar or tube, so that if a motion of turning is given to the supporting tube all the rings turn at the same time, the points come down and the goods fall off them by their own weight. This ingenious arrangement is one of the most interesting in connection with the apparatus.

"According to information communicated by M. Sifferlen, he can steam 20 pieces of 45 metres at one time; in an ordinary steaming vat with a square section of 1 m. 60 about, there can be steamed 6 pieces each of 100 metres, which

comparing the section is about the same result. As to the manipulations preceding the steaming, it takes thirty to thirty-five minutes in M. Sifferlen's arrangement to hook on 900 metres; the rolling-on of 600 metres by the old process takes at least twenty minutes.

"The kind of steaming box described by M. Sifferlen is very little known in this district."

Bismarck Brown on Wool, Light Shade.—One-half per cent. of the weight of the wool of good Bismarck brown is required to give a dark shade, and less for lighter colours; the necessary quantity is dissolved in warm water and filtered, then added to the dye water, which is heated to about 170° F., and contains about 1 lb. glauber salts (sulphate of soda) to 10 lb. of wool to be dyed; the wool is entered and the liquor slowly brought up to the boil.

Iodine or Methyl Green for Printing on Cotton.—A thickening is made from starch along with a little tragacanth, and a standard liquor made by dissolving the green in water along with about twice its weight of oxalic acid, and adding four times its weight of tannin, with a little acetic acid. The strength of the standard and the proportion to be added to the thickening depend entirely upon the quality of the green and the shade of colour required; fix by steaming.

Mordant for Alkali Blue on Cotton.—One pound of olive oil mixed with 10 oz. of strong sulphuric acid, stir well up for some time, and add one pound methylated spirit. Dilute with hot water, and add 3 oz. of bichloride of tin. In mordanting mix this compound with the requisite amount of water at about 100° F., and work the cotton in for one hour; the above quantities being adapted for 20 lbs. cotton yarn. Dye as usual.

Change of Cotton into Glucose and Dextrine.—Kosmann, in studying the action of oxidizing agents upon glycerine and

other organic matters, has found that pure cotton in contact with aqueous solution of permanganate of potash is partially transformed into glucose and dextrine; bichromate of potash alone or mixed with acetic acid has a similar action. By leaving cotton in contact with iron and water for thirty-one days, this observer found that a portion of the cellulose was changed into glucose and dextrine, besides which there was a certain amount of a gummy matter formed, which did not become blue with iodine, but was changed into glucose by the action of boiling sulphuric acid. Solution of bleaching powder, acting upon cotton until it was dissolved, yielded glucose, dextrine, and formic acid combined with lime.—*Bull. de la Soc. Chem., October 5th, 1877.*

Prussian Blue on Wool and Silk.—In a description of Bang's French patent it is said the aim of the process is to use up almost completely the total quantity of cyanogen contained in the prussiate in the formation of the blue colour, and thus avoid the dangerous emanations of prussic-acid vapour. For this purpose the patentee uses a mixture of red prussiate and per-salt of iron, equivalent to equivalent, or in various proportions according to the shade of colour required. It is therefore, he says, in reality a ferricyanide of peroxide of iron which he employs; the salt is perfectly soluble, fixes gradually upon the wool or silk, and is changed by the heat of dyeing into an insoluble colour; at the same time the yield of colour is nearly double of that obtained from prussiate used in the ordinary way.—*Mon. de la Teinture, October 5th, 1877.*

Colouring Matter from Tar.—A German manufacturing company (*Chemische fabrik echter farben Actien Gessellschaft*) has patented in France a new colouring matter obtained by separating from tar the heavy oils, and especially those which have a yellowish and turbid appearance, for these contain the colouring matter in question. Caustic potash or other alkali is used to isolate it, and then the oils are combined with potash and quick-lime, and the dry mass strongly pressed to separate the insoluble oleate of lime. The liquid, which is a mixture of oil and alkali, is concentrated and exposed to the

air supported on cloths to oxidize it, or until it becomes distinctly blue. The colouring matter is afterwards extracted and purified by repeated solution in acids and precipitation by alkalies; the product is a violet colour, but is a base which can be modified by suitable reagents so as to yield many kinds of colours.—*Mon. de la Teinture, October 5th, 1877.*

Albumin of Commerce.—Under this title Messrs. Charles T. Kingzett, F.C.S., and M. Zingler communicated a paper to the recent Pharmaceutical Conference describing their patent for preparing blood albumen, the specification of which appeared in a late number of the Textile Colourist. The paper is printed in the Pharmaceutical Journal of September 29th, 1877, p. 253, and commences as follows:—"As is well known, albumin is largely employed for fixing colours on cotton goods, such colours for instance, as madder red and indigo blue, which are almost the only fast colours possessed by dyers. For fixing these and other colours egg albumin is well adapted," etc. This is an extremely bad shot on the part of the learned authors of the paper, for madder red and indigo blue are precisely the colours for which albumen is never used, and never has been used.



5. *British and Foreign Patents, from the Commissioners of Patents Journal, October 30th, 1877, to November 23rd, 1877, inclusive.*

Colouring Matters.

3731. HEINRICH CARO, Chemist to the Badische Aniline and Soda Works, of Mannheim, in the empire of Germany, has given notice to proceed in respect of the invention of "Improvements in the production of colouring matters suitable for dyeing and printing."
3737. REINHOLD HOFFMANN, of Marienberg-bei-Bensheim, in the empire of Germany, Chemist, has given notice to proceed in

- respect of the invention of "Improvements in the production of colouring matters."
3742. THOMAS HOLLIDAY, of the firm of Read, Holliday, and Sons, of Huddersfield, in the county of York, Manufacturing Chemists, has given notice to proceed in respect of the invention of "Improvements in dyeing textile fibres black or grey colours with aniline."—A communication to him from abroad by William Jules Samuel Grawitz, of 1, Boulevard Henry IV., Paris, in the republic of France.
3751. HEINRICH CARO, Chemist to the Badische Aniline and Soda Works, of Mannheim, in the empire of Germany, has given notice to proceed in respect of the invention of "Improvements in the production of colouring matters suitable for dyeing and printing."
3757. MAXIMILIAN ZINGLER, of 19, Buckland Crescent, Belsize Park, in the county of Middlesex, for an invention of "Improvements in treating aniline and other dyes to prepare them for use in dyeing, printing, and colouring."—Dated 30th October, 1874.—This patent has become void.
- 117,768. MOUZIN, of Tergnier, for "Obtaining red and black colours from the raw black ashes or red ashes of alum-works."—Dated 4th April, 1877.—French patent.
1. J. ZELTNER, of Nürnberg, for "Obtaining violet ultramarine."—Dated 17th September, 1877. German patent.

Dyeing, Printing, Singeing, Drying.

4101. GEORGES CHALAMEL, of the firm Alfred Chalamel et Ce., of Puteaux (Seine), Manufacturer, for an invention of "An improved apparatus for dyeing, with preserved parts, wool and other fibrous substances."—Dated 5th November, 1877.—Provisional protection has been granted.
1900. P. BARTHEL, of Frankfort-on-the-Maine, for A. A. Plantrou, jun., of Rheims, for "Scouring and cleaning textiles."—Dated 18th October, 1877.—German patent.
- 117,632 DAVID, for "A machine for embossing and printing ribbon and plain velvet stuffs in various colours at once."—Dated 24th March, 1877.—French patent.
- 117,762. VIGNE', sen. and jun., for "Obtaining embossed velvet with designs of various colours."—Dated 4th April, 1877.—French patent.

- 117,838. WINTER, for "Improvements in producing photographic pictures on tissues."—Dated 31st March, 1877.—French patent.
- 193,158. WILLIAM J. S. GRAWITZ, of Paris, France, for "Dyeing yarns and fabrics in aniline-black."—Patented in England, 21st October, 1874, for fourteen years.—Application filed 13th March, 1877.—United States patent.
3636. SAMUEL KNOWLES, of Tottington, near Bury, in the county of Lancaster, Bleacher and Calico Printer, and JAMES KAY, of Bury aforesaid, Engineer, for an invention of "Improvements in apparatus for drying yarns, woven fabrics, paper, and other materials."—Dated 22nd October, 1874.—This patent has become void.
3812. WILLIAM SUMNER, of Salford, in the county of Lancaster, and ERIC HUGO WALDENSTRÖM, of the same place, Engineers, for an invention of "Improvements in the manufacture of copper singe plates."—Dated 4th November, 1874.—This patent has become void.

Wool Treatments.

2208. ANDRE PROSPER ROCHETTE, of Petit-Quevilly, près Rouen, in the republic of France, for an invention of "Improvements in washing wool, and in solutions employed for this purpose."—Dated 6th June, 1877.—Sealed November 2nd, 1877.
4227. WALTER ALFRED BARLOW, of 6, St. Paul's Churchyard, London, Patent Agent and Engineer, for an invention of "Improvements in means and apparatus for removing or destroying vegetable matters from or contained in wool, woollen rags, or woollen cloth."—A communication to him from abroad by C. F. Gademann, Manufacturer, of Biebrich-on-the-Rhine."—Dated 12th November, 1877.
4095. JOHN CLOUGH, of the Manchester Road, Bradford, in the county of York, for an invention of "Improvements in apparatus employed in the washing and cleansing of wool and other fibres."—Dated 30th November, 1874.—The £50 stamp duty has been paid.
- 117,608. CAZANAVE, for "Burring wool and removing ligneous substances therefrom."—Dated 19th March, 1877.—French patent.
- 117,726. JOURDAN, of Balan, for "Cleansing wool by means of anhydrous gas."—Dated 29th March, 1877.—French patent.

2723. C. L. SCHULTZE, of Berlin, for "Obtaining greenish blue on wool."—Dated 2nd October, 1877.—German patent.

Yarn Treatments.

4149. ANDREW MUNGALL, Manager, Dalmarnock Dye Works, Glasgow, in the county of Lanark, North Britain, for the invention of "Improvements in the separating or splitting of warp yarn into single chains or webs after dyeing, washing, or bleaching, and in the machinery or apparatus employed therefor."—Provisional protection has been granted.
4377. THOMAS PATERSON MILLER, of the Cambuslang Dye Works, in the county of Lanark, North Britain, for an invention of "Improvements in apparatus for dyeing yarn or thread."—Dated 21st November, 1877.
1847. O. GREINER, of Berlin, for "A wringing machine for yarn in skeins."—Dated 24th September, 1877.—German patent.
869. C. G. HAUBOLD, jr., of Chemnitz, for "Machines for dyeing and impregnating yarn in skeins."—Dated 17th September, 1877.—German patent.

Finishing Operations.

1994. WILLIAM WALTON URQUHART and JOSEPH LINDSAY, both of Dundee, in the county of Forfar, North Britain, Engineers, for an invention of "Improvements in machinery or apparatus for treating or finishing woven fabrics."—Dated 22nd May, 1877.—Sealed November 16th, 1877.
2239. GUSTAVE HERTZOG, of Reims, France, Mechanic, for an invention of "Improvements in tenter-hooks or grippers for self-acting or other stretching machines for textile fabrics."—Dated 8th June, 1877.—Sealed November 22nd, 1877.
4368. WILLIAM BIRCH, of Salford, in the county of Lancaster, Machinist, for an invention of "Improvements in machinery for guiding, opening, and stretching fabrics during bleaching, printing, or other manipulations."—Dated 21st November, 1877.
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MANCHESTER :
PALMER AND HOWE, PRINTERS, BOND STREET.

with the tin mordant, cream of tartar, and a small quantity of cochineal first, and then a second time with less tin mordant and tartar, and the remainder of the cochineal; looser or opener materials, as flannel or yarn, can be dyed at once, as in the following practical process for 60 lb. weight of flannel:—Take 5 lb. tartar, 6 lb. ground cochineal, and if the shade is wanted yellowish, 8 or 9 oz. of flavine; if wanted crimson hued, only 2 or 3 oz. of flavine, 3 half-pints of single muriate of tin, and $4\frac{1}{2}$ quarts of nitrate of tin (this nitrate of tin made by dissolving 30 ounces of feathered tin in 20 lb. of nitric acid at 33° or 34° Tw.) Put all into the dyeing vessel with the requisite amount of water, and boil up together; enter the goods and work them in the dye for forty minutes, examine the woollen, and if deficient in colour, add 1 or 2 lb. more of cochineal, with 1 part of nitrate of tin to each pound of cochineal, flavine if necessary, and with it some muriate of tin; boil for twenty minutes more, wash, run for ten minutes in water containing fullers' earth, wash, and dry.

Bancroft states that an ounce of fine cochineal is generally deemed sufficient for one pound of cloth, but this proportion will vary according to the quality of the cochineal and the nature of the cloth.

The introduction of a yellow colouring matter along with cochineal to economise it is due to Bancroft, who succeeded in proving, after many costly experiments, that it could be safely and

profitably used. His method was, to dye the cloth at first a light yellow with quercitron bark and sulphomuriate of tin, afterwards dyeing with cochineal and tin as usual. It was Bancroft's opinion that the cochineal was turned to a scarlet hue by the tartar used in dyeing, and that by using a yellow colouring matter the tartar could be dispensed with. The use of quercitron bark or fustic did not become general in scarlet dyeing until about 1812. It has been found, however, that tartar cannot safely be dispensed with, although somewhat less may be used than was previously employed.

Crimson and cherry colours upon wool are obtained by using a certain proportion of ammoniacal cochineal along with ordinary cochineal, the other materials and the process being the same as for scarlets, except that sometimes alum is added to the dye liquor. The shade tends more and more to the blue side as the proportion of alum and ammoniacal cochineal is increased. Pink colours upon wool are obtainable from the ammoniacal cochineal alone with alum and tin for mordant. Cochineal dyes very well upon silk with a simple muriate of tin mordant, the bichloride being usually employed; the shades from crimson to pink being produced by simply using different proportions of the colouring matter to a given weight of silk.

With iron mordants cochineal gives lilac or purplish shades of colour, but they do not possess any especial beauty and are seldom worked,

Lac-dye.—This substance finds its place here not only as being a red colouring matter, but also because it is produced by an insect very similar to the cochineal insect. Bancroft considers that it was probably unknown in Europe until after the Portuguese had visited India by sailing round the Cape of Good Hope. But from Merrifield it seems certain that the Indian lac was imported into Spain and Provence as early as 1220, and used as a dyeing material then and ever since. In the Paduan manuscript, quoted by the last author, the method of extracting the colouring matter by means of a ley of wood ashes is described at length. At early periods the Indian lac appears to have been esteemed only for its colouring matter, its value for varnishes and as a gum resin was only utilized at a comparatively modern date. At the present time the colouring matter is of secondary importance compared with the resinous matters accompanying it.

As the lac is collected from the trees or shrubs upon which it grows, the amount of resinous matters greatly exceeds that of colouring matter, the insect being surrounded and buried in a mass of resin which its puncture has caused to be formed all around it. In very dark specimens of stick-lac Bancroft estimated there was as much colouring matter as is equivalent to one-sixth of its weight of fine cochineal; but lighter specimens, those of an amber colour, were not equal in colouring power to more than one-fifteenth of their weight of cochineal, the average dyeing power being equal to about one-tenth of the weight of

cochineal. It does not appear that the extraction of the colouring matter and its preparation as an article of commerce dates further back than 1798, when Bancroft received a specimen of lac-lake from India which he found to contain alumina, and which by proper treatment dyed up better colours on wool than any extract he could himself prepare from the natural lac. This author states that prior to 1798 a company had been formed in England for preparing an extract of the colouring matter from stick-lac, but it did not succeed. The colour is soluble in pure water, in acids, or in alkalies, and soon after Bancroft's experiments an extract of it began to be imported from India in large quantities under the name of lac-lake, and it is stated that the sales of this material at the India house in the three years ending 1813 were so large, that in point of colouring matter the quantity sold was equal to half-a-million pounds weight of cochineal, but the quality was so irregular that after a while it fell into disfavour with the dyers and ceased to be used by them, and this apparently because the Indian extractors used an alkaline solution to dissolve the colouring matter, which at the same time dissolved so much of the resin as to produce stains upon the cloth in dyeing. This inconvenience is in a great measure obviated by the existing methods of using the lake.

The earliest account of the method of practically applying lac-lake with which I am acquainted is in the patent to Wright, dated December 9th, 1813, which is entitled "An improved method of making a

composition or mixture for dyeing scarlet and other colours." The mixture is composed of 26 parts lac-dye, 40 parts lac-spirit or solution of tin, 26 parts cream of tartar or argol, 1 part turmeric, 2 parts cochineal, 4 parts extract of safflower, and about 1 part sulphuric acid. In the *Annals of Philosophy*, for 1826, a more detailed process is communicated, applicable to an improved quality of lac-lake at that time imported from India.* The lac-lake was mixed in the proportion of 1 lb. of it to $\frac{3}{4}$ lb. lac-spirit, made from 60 lb. muriatic acid and 3 lb. tin; 4 oz. of another solution of tin afterwards added (made from 28 lb. nitric acid at sp. gr. 1.170, with one-twentieth part of hydrochloric acid and 4 lb. tin gradually dissolved), the mixture being left six hours. For 100 lb. thin and open woollen cloth a vessel of three hundred gallons capacity was used with sufficient water, the water heated to 150° F. and a dishful of bran and half-a-pint solution of tin added; this purifies the water, causing a scum to arise which must be removed. The temperature being then raised to the boil, 10 $\frac{1}{4}$ lb. of the lac-dye, previously mixed with 7 pints lac-spirit and 3 $\frac{1}{2}$ pints nitrate of tin mordant, are poured in, immediately afterwards 10 $\frac{1}{2}$ lb. tartar are added and 4 lb. young fustic in a bag, the boiling continued for five minutes, then 20 gallons cold water added with 10 $\frac{1}{2}$ pints more of the nitrate of tin, the cloth entered and boiled one hour. The cloth in this case weighed 12 oz. per yard; heavier stuffs take less dye, because it

* Vol. xxvii., p. 401, April 26th, 1826.

does not enter so completely into the material, for example the $10\frac{1}{4}$ lb. lac-dye is sufficient for 140 lb. of cloth weighing 24 oz. to the yard. For a small trial dye, the following proportions may be used:—180 grains woollen yarn in a six-pint vessel, 60 grains lac-dye, 40 grains lac-spirit, 40 grains nitrate of tin; and in the dyeing, 70 grains tartar, 1 dram tin, and 12 grains young fustic.

The following method of treatment is substantially the one given by Grison in his treatise upon woollen dyeing, 1860.

The lac-lake is reduced to fine powder by grinding and sieving, then 15 lb. of it are mixed with an equal quantity of water, and 12 lb. oxymuriate of tin in an earthenware vessel, the whole is mixed up to a uniform thin paste and well stirred about for the space of an hour, it may be ready for use in twenty-four hours, but some dyers prefer to leave it for a week so that the action may be thoroughly completed; this mixture is said to become injured if left longer than fifteen or twenty days, giving duller colours. Before dyeing it is mixed up with boiling water, in some instances the whole mixture is put into the dyebeck, in other cases it is directed to employ only the clear liquor. Instead of the acid salt of tin, simple hydrochloric or diluted sulphuric acid may be used, the object being really to liberate the colouring matter from the alumina or other bases with which it has been precipitated in the manufacture of the lake.

The mordanting and dyeing are exactly the same as

for cochineal, in a given instance (from Grison) 10 lb. of merino are worked for half-an-hour in water, along with $1\frac{1}{2}$ lb. tartar and $1\frac{1}{2}$ lb. oxymuriate of tin, and then a quantity of prepared lac-dye, equal to $1\frac{1}{2}$ lb. of the dry lake, is added to the dye and the cloth kept in at near the boil for forty-five minutes. For finer shades of colour the cloth is topped by another slight dyeing in cochineal, with addition of flavine or fustic if the shade requires it.

The older writers were of opinion that the lac colours were faster than the cochineal colours though not so bright, this idea is probably not correct, for when care is taken to obtain a very pure extract of the lac-dye the colours appear to be exactly the same both in fastness and brilliancy as those yielded by cochineal. The attempts which have been made to use lac-lake in printing, as a substitute for cochineal, have not been successful. Although the real value of a sample of lac-lake can only be ascertained by an actual dyeing experiment, a comparative estimation may be made from the external appearances of samples, those being preferable which are apparently most free from resin, which break easily in the fingers with a dull fracture; hard samples which give a bright fracture may be judged to contain a large proportion of resin.*

* A lac-lake, prepared in England by Brookes' process, is highly spoken of by several authorities; reference may be made to Henley's patent, December 30th, 1868, in which it is said the colour can be extracted from lac-resin by pressing it in bags at a temperature of 300° F., the resin comes out and the colouring matter remains in.

Kermes.—As previously mentioned, this substance was in use in Europe for dyeing scarlet and crimson colours before the discovery of cochineal. It is still used in remote places where dyeing partakes more of a domestic than a commercial occupation. Its colouring principle is probably identical with that of cochineal, since it yields the same colours possessing an equal if not a greater degree of stability; but, compared with cochineal, it is poor in quality of colouring matter, and has for this reason been neglected and almost forgotten in the chief markets of the world. Chaptal states that one person could collect from 1 lb. to 2 lb. of kermes in the course of a day, but it is estimated that it would take 12 lb. to equal 1 lb. of cochineal in dyeing power; it is not, therefore, worth the labour of collecting. The insect, according to Kirby and Spence, lives only on the *quercus coccifera*—a low evergreen oak, with prickly leaves. It does not appear that it has ever been the subject of systematic cultivation like the cochineal insect. In point of antiquarian interest there is no colouring matter or other material used by dyers which can equal kermes. From the researches of scholars skilled in the ancient Oriental languages, it would seem demonstrated that the existence and use of this dyestuff can be traced to the most remote period which can be embraced in the historical period, and it is even dimly discerned beyond that. It is mentioned in the Hebrew scriptures. It was evidently used by Phœnician and Egyptian dyers before

the time of Moses, and is believed to have been the source of the red colours upon silk used to ornament the tabernacle of the Israelites in the wilderness. It is plainly distinguished in the most ancient writings from the Tyrian purple, and is older than it. Later on it is found mentioned by Greek and Latin authors, and some of its uses described. The present name is Arabic, and, like cochineal, its appearance caused it to be commonly considered a berry, and was like it called *grain*, whence is derived the terms of "colour in grain" or "ingrained colours" for fast and durable colours. From kermes also probably comes the name of crimson, and further vermilion, from the Latin for the worm or insect yielding the colour so designated.*

There are other insects which give a red colour in dyeing, as the *coccus polonicus* and *coccus uvae ursi*, but they are of no practical or commercial importance.

The Red Woods.—After the red colouring substances treated of, the next in importance are what are called the redwoods, which are a class of solid, compact, and hard woods from trees of considerable size. These woods contain a colouring matter which gives reds with alumina and tin mordants. The redwoods may, from a dyer's point of view, be divided into two classes—those of which the colouring matter is easily and largely soluble in water, and those whose colouring matter is very slightly soluble in water. Brazil wood may be considered the type of the first class and barwood that of the second.

* See Bancroft, i., p. 393; and Beckmann, ii., p. 185.

Brazil Wood.—This wood is of very old use in dyeing; it was known to the ancient Hebrews and to the Arabs. The old Italian dyers called it *verzino*, and Marco Polo states that the best quality grew in the island of Ceylon. Processes of using it for dyeing skins and for making a lake for artists are frequently given in books and manuscripts of the fourteenth century and later. Its name can be traced as early as 1194, and is supposed to be derived from a French word, signifying a flame or fire colour. Soon after the discovery of America, and about the close of the fifteenth century, one of the most striking events was that the explorers found whole forests in which are none other trees than Brazil, which the Italians call “*verzino*.”* The precious trees were immediately felled in great numbers, their value being well understood and preparations made for their transport to Europe. The various places in which these trees abounded were called Brazil, from the wood; but it was nearly one hundred years afterwards before the term became definitely affixed and limited to that country south of the equator which now constitutes the empire of Brazil.

Besides Brazil wood proper, there are other red woods from the same kind of tree growing in different parts, and known in England as peachwood, sapan wood, Lima wood, etc.; the colouring matter in these variously-named woods is probably identical, and their differences in value or more or less fitness for

* Report of Peter Martyr. See Bancroft, ii., 318; and Merrifield, i., clxxx.

certain uses, is owing to a greater or less richness in colouring matter, and the existence or absence of foreign or useless constituents. These woods have not, however, been rigorously examined by chemists, and our information is defective as to the colouring principles and other matters they contain. Brazil wood yields a crystalline colouring principle which has been called Braziline.

In calico printing, extracts of the red woods are principally used for sightening mordants and for steam colours. The ground wood is rather largely used in the lower class of garancine dyeing as a cheap substitute for garancine; it gives the same kind of colours as garancine to mordants, but of a greatly inferior quality in every respect. As a dyestuff or colouring matter by itself, the red wood is but little used in any kind of dyeing, the colours it gives possessing but a small degree of permanency. As a red part in compound colours, it is very valuable in many cases. Lake from Brazil wood and similar red woods is much used in paper printing.

The chief cases in which the red woods come into use in calico printing may be stated as follows:— Steam reds and pinks of a low class on calico were formerly somewhat largely used. A capital improvement on this class of reds, and in fact for all the compound colours in which decoctions of the red woods are employed, was discovered many years ago by Mr. Ashworth, then at Messrs. Knowles', of Tottington; it consisted in the addition of chlorate

of potash to the usual ingredients of the colour, and was probably the first instance in which this salt was employed in calico printing. The nature of its action is obscure, but it most probably acts as an oxidising agent, and its utility has been universally recognised. The manufacturers of the red extracts (sapan liquor, peachwood liquor, etc.) formerly added chlorate of potash to the extracts, and may do so yet, but it is generally found advisable for the colour mixer to use some in the colour, say from 2 to 4 oz. per gallon of the red extract. The proper mordant is alum for reds and salt of tin for pinks, generally in the latter colour in conjunction with copper salts, which no doubt have an oxidising action. In some red colours, nitrate of alumina figures largely; here also an oxidising influence may be reasonably assumed, it being observable with the red wood in every way in which it is applied that it seems to require oxidation, hence old liquors are preferred to those recently prepared.

The chief use, however, of the red wood extracts was and is in steam chocolate colours for calico, wool, and delaine, especially for the red shades of chocolate in which the red woods predominated; as for example, in the following illustration for delaine:—20 gallons of sapan wood liquor at 14° Tw., thickened with starch and gum substitute, and when somewhat cool, the following salts dissolved in the mixture; 4½ lb. chlorate of potash, 10 lb. alum, and ½ lb. oxalic acid. To the colour thus prepared, a certain proportion of a logwood colour

was added, the logwood colour giving a purple; the mixture of it with the red produced the chocolate, and according to the particular shade of chocolate required, the logwood part was increased or diminished.

For woollen dyeing the soluble class of red woods are very little employed, for silk dyeing they answer somewhat better.

Barwood, Camwood, etc.—The class of red woods of which barwood may be considered the representative and type, appear to have a resinous colouring matter; the colouring principle is soluble in water, but only to a very small extent, so that it is not possible to obtain the usual strong decoctions as in the case of peachwood or sapan wood. These woods are consequently not used in colour mixing, but they are somewhat extensively employed in dyeing, for which purpose they are rasped and ground as fine as possible. Upon cotton they yield, with a tin mordant, a good shade of red, possessing fair stability, which, from its resemblance to Turkey red, is not unfrequently substituted for it when a low-priced article is required. In wool dyeing these woods are much more employed than the more soluble red woods, giving dull red and red-brown colours with the ordinary alumina and bichromate mordants, and with iron mordants in addition, heavy red brown shades, which are esteemed for their permanence. They are also valued as giving the best bottom for indigo-dyed woollens. Saunders wood, or red sandal, and caliatour wood belong to this class.

In the patented processes referring to barwood the following may be noted:—Roberts and Dale patented July 17th, 1857, a method of obtaining red lakes principally for application to paper printing. The barwood was heated to boiling along with persulphate of tin, which fixed the colouring matter as it was extracted by the water, forming a lake which could be separated by subsidence and sieving. Dale, on March 24th, 1860, patented a method of extracting the colour from barwood and camwood by using a definite amount of alkali, avoiding an excess which is destructive. For one ton of barwood he employs 120 lb. caustic alkali at 25 per cent. diluted with 500 to 800 gallons of water, this gives a red and not a purple solution. When cool the solution is precipitated by acid and the colouring matter collected in the usual way. Ashton's patent of May 29th, 1862, is for using the wood in dyeing. To prevent the inconveniences attending the contact of the wood and stuff in the usual method of dyeing he places the dyewood in a false bottom formed of perforated metal or wire gauze. Hall and others have a patent dated September 27th, 1869, for an apparatus for shaking the adhering dyewood from yarns dyed with it, so as to avoid the inconveniences of the common method of shaking it out by hand.

Safflower.—Although this dyestuff is chiefly employed for giving a pink colour, it may be considered among the red colouring matters. It consists of the petals of a plant which grows in Egypt, India, and in

most countries of a semi-tropical climate, as Spain, Persia, etc. As imported for the dyer's use, it is found to contain a large quantity of a yellowish colouring matter which is of no value. This is fortunately very soluble in water, while the valuable red colouring matter is not. The first operation in safflower dyeing consists in treating it by some convenient apparatus with cold water until it is purified from the soluble principles it contains, and then extracting the red colouring principle by weak alkaline solutions. This washing out of the yellow and dissolving the true colouring matter from the safflower is an operation best done just as the colour is wanted, and immediately before its application to dyeing. The goods to be dyed—say calicoes for linings—are then worked in the cold alkaline solution of the colouring matter; and when well saturated the bath is made acid by tartaric acid, citric acid, or sulphuric acid, and the goods again worked in; the acid neutralizing the alkali, changes the colour of the solution from buff to pink, rendering the colouring matter insoluble, and precipitating it upon the fibre, to which it adheres well and evenly, and may then be washed in clean water to remove the salts. The only cause of unevenness or uncertainty in this simple method of dyeing will reside in impurity of the cloth or the alkaline nature of the water. If safflower-dyed cottons be washed off, after dyeing, in a water containing much bicarbonate of lime, and dried up from this water, they will probably lose shade, and become

yellowish. With such a water the goods must either be not washed off at all, or they must be finally rinsed in water very faintly acidulated with tartaric or some other suitable acid. For fine shades on silk the safflower is submitted to a more careful purification from the yellow colouring matter, and is even sometimes dissolved off from cotton for the purpose. A prepared extract of safflower is much employed by small dyers who have only occasionally to dye this colour. The safflower pink has a beautiful and agreeable hue quite peculiar to this material; in later times it has been closely approached, but not actually equalled, by some of the artificial colouring matters. It is a very fugitive, unstable colour, having no fastness against soap, and easily injured by light and air; its applications are consequently limited to fancy articles, in which beauty is of greater importance than durability. It is a somewhat costly dyeing material, and wherever it can be assisted by the conjunction of less expensive colours, such as cochineal, annatto, or archil, the dyer takes advantage of their aid.

Archil and Cudbear.—These dyestuffs though not precisely or exclusively red colouring matters, are more appropriately treated in this place than in any other. They are manufactured products of various lichens or marine algae. Their use as tinctorial substances was known to the ancient Greeks and Romans and then for several centuries was forgotten, and rediscovered or revived in the year 1300 in Italy by a

family who retained the secret for a long time and acquired great wealth by their use of these substances in dyeing. It would be superfluous here to go at length into the manufacture and chemical history of the various lichens yielding colouring matters; it is sufficient to state that though colourless at first, these plants develop colour either spontaneously by being kept in a warm place, or more quickly under the influence of ammonia, which was in all the older processes derived from decomposed human urine. In the modern process of preparing the common paste archil the weed is simply ground up with liquid ammonia for several days with a regulated access of atmospheric air; in the earlier stages of the contact of the weed and alkali blue archil is produced, a more prolonged contact with air and ammonia yields the red archil. Archil liquor is prepared from a decoction of the weed heated and mixed with ammonia. Cudbear does not appear to be anything but paste archil dried and ground to a fine powder. More scientific processes have been proposed for obtaining the colouring matter in a purer state, but whether they have been practically successful is not known, the manufacture of these articles being carried on with real or pretended secrecy.

For cotton goods archil has no affinity or attraction unless applied with albumen or lactarine, and at this date (1877) is not in use; for woollen and mixed goods archil is used in steam colours for shades of chocolates, which are rich and beautiful; it dyes wool without

mordants various shades of red inclining to purple, but it is usual to prepare the wool with either alum or tin mordant, but for archil alone nothing except a certain degree of acidity is required, which can probably be best obtained by addition of oxalic acid or acid oxalate of potash. The chief use of archil in wool dyeing, as in wool printing, is for the production of compound shades of the brown and chocolate class of colours, in which it is used in conjunction with sulphate of indigo, logwood, fustic, turmeric, and other colouring matters and appropriate mordants; in all these colours the use of archil gives a fulness and richness which cannot be obtained by the use of any known substitute, this quality, combined with regularity and certainty of result, makes it a very valuable material for the woollen dyer.

About the year 1857, a preparation of archil was introduced, under the name of French purple. The commercial article was actually a combination of lime with the colouring matter of archil, and not only was it capable of yielding very fine shades of colour, but the colour was greatly superior in fastness to any previously known preparation of archil. From the process of its manufacture, as described by the inventors, it would appear that this improvement resulted from keeping the solution of archil at a temperature near the boiling point of water for a considerable length of time. The French purple was applied in calico printing by means of albumen, and it would probably have had a successful run, but

just at that time aniline mauve came into the market, and so to speak, completely extinguished it. De Claubry states that fast archil was discovered by Hélaïne, of Lyons, and it was made by adding ammoniuret of tin to dissolved commercial archil. This so-called ammoniuret of tin is made by adding an excess of ammonia to oxymuriate of tin, draining the precipitated paste, and dissolving it in strong ammonia. The addition of the alkaline tin solution produces a précipitate, which, when washed, is the fast archil; it requires the addition of acid in dyeing. Grison claims a great superiority for a preparation of archil discovered by himself, which he calls archil carmine, or archil extract, and which is made as follows:—Take 100 lb. of common archil several months old, and mix it with 10 gallons of water and 20 lb. of strong sulphuric acid in a wooden tub; mix well and boil up for two hours by means of a steam pipe, then add 40 gallons water and boil for fifteen minutes, filter to separate the soluble and insoluble parts, wash the insoluble matter with boiling water three times to exhaust it. Neutralize the acid in the united liquors by addition of strong ammonia, which must be used in quantity sufficient to give a slight alkaline reaction and a violet colour. An abundant precipitate is formed which is allowed to deposit. The precipitate is collected and washed with hot water to remove a brownish colouring matter present in it; the washed paste constitutes the improved archil. To use it for dyeing it is dissolved

in hot water along with bioxalate of potash, filtered, and the clear liquid used for dyeing.*

Among the patents referring to archil and cudbear, the following may be cited as of interest:—In a patent to Abraham Kemp, in 1693, for making “orchall and litmus,” these materials are mentioned as being useful in scarlets, crimsons, claret colours, blues, and others. The production of cudbear is patented by George Gordon and Cuthbert Gordon, August 12th, 1758. No details of its preparation are given, but it is said to be “for a valuable and beneficial dye which we call cudbear, to be used as a substitute for archil or Spanish weed, and is entirely composed of materials the produce of Great Britain or of His Majesty’s plantations.” In 1849, February 14th, Chaudois patents the treatment of the washed products of lichens instead of the whole mass. The washing may be with water only, or with alkali and urine. Robinson’s patent of August 30th, 1849, is for contrivances for dividing the paste of lichens so as to facilitate the action of the air upon it. This is done by forcing the pulpy mass through small openings, the operation being repeated twice a day for three days. In this patent cudbear is spoken of as paste archil dried and ground. In 1850, January 3rd, Lightfoot patented the printing of archil colours upon cloth prepared with oil. Murdoch’s patent, October 9th, 1855, is for the extraction of the colouring matter of the lichens in a

* *Repertoire de Ch. App.*, i., pp. 189, 253; Grison, *Teinturier*, etc., p. 256; *Technologiste*, xxi., p. 126.

distillatory apparatus by means of alcohol or ammonia. Brooman's incompleated patent of September 6th, 1860, is for blowing air or oxygen gas through an alkaline decoction of the lichens. Barry, on February 20th, 1850, patented the application of the lichens growing upon apple and crab trees for dyeing brown colours as a new discovery made by him.

Adulteration and Testing of Archil.—The quality and purity of a given sample of archil or cudbear can only be satisfactorily ascertained by the practical dyeing test. Leeshing says* that he has found archil adulterated with logwood, and that the dyeing test does not clearly shew this adulteration. To examine for it he recommends an acid solution of protochloride of tin to be added to the suspected archil in mixture with water and heated to boiling. If pure, the archil is nearly decolourized, but if logwood or other woods be present, characteristic shades of colour are produced. He moreover adds, that blue archil acquires all the properties of red archil by addition of a small quantity of red prussiate of potash. According to Stenhouse, who is a high authority upon the colouring matters in lichens, the amount of real colouring matters can be accurately estimated by the following process.† One hundred grains of the lichens to be tested are macerated with a dilute solution of caustic soda, two treatments being sufficient to extract the whole of the colouring matter. A solution of hypochlorite of soda of a known strength should be added

* Ch. Gaz. xiii., p. 219. † Journ. of Ch. Soc., xx., p. 226.

to the solution from a graduated alkalimeter, the moment the bleaching liquor comes into contact with the solution of the lichens a blood-red colour is produced, which disappears in a minute or two, and the liquid retains only a deep yellow colour. A fresh quantity of the bleaching liquor should then be poured into the solution and the mixture carefully stirred. The operation should be repeated so long as the addition of the hypochlorite causes the production of the red colour, for this shews that the solution still contains unoxidized colouring matter. Towards the end of the process the bleaching solution should be added by only a few drops at a time, the mixture being carefully stirred between each addition. We have only to note how many measures of the bleaching solution have been required to destroy the colouring matter in the solution to ascertain the amount of colouring matter it contained. Another method by the same authority consists in exhausting the lichen with milk of lime, precipitating with acetic acid, collecting the precipitate on a weighed filter, drying it at the ordinary temperature, and then weighing it. In this way the amount of colouring principle is directly determined, but it is tedious and difficult for any one but a chemist to perform; the method above given is more practical.* According to Gaultier de Claubry, lichens do not give more than 10 to 12 per cent. of utilisable colour.

* See also de Luynes, *Compt. Rendu*, lxxvii., p. 239; *Technologiste*, xxv., p. 21; xxx., p. 18; and xxiii., p. 32.

There are no other red colouring matters which need occupy space in a work which is only concerned with those practically applied. At the end of the book will be found references to others of little practical importance, such as alkanet, chica, sorgho, and murexide. As a pigment red colour lately applied in indigo discharge styles by means of albumen, vermilion may be mentioned; it is not, however, likely to be a useful pigment. There is a great want of a good red pigment colour, none of a satisfactory nature having yet been discovered.

BLUE COLOURING MATTERS.

Indigo.—This is the most important of the blue colouring matters, and probably the most important and valuable of all the colouring matters employed in dyeing. Unlike the majority of dyestuffs, it comes into the market in a manufactured state, and probably has always done so. The plant which yields it contains but a small proportion of colouring matter,* and is, besides, very bulky. Fortunately the colouring matter is very easily extracted by water alone, and can be precipitated and collected as a dry substance containing as much as 60 per cent. of pure colour. If it was not for this it would, like madder, have to be exported in the bulk, at much greater cost and risk of injury than it has to encounter in its present well-known form.

* According to Roxburgh 250 lb. of the green plant yields only 1 lb. of indigo, but it varies.

Blue colours obtained from indigo-yielding plants have been known and utilised from the remotest ages, and in all countries possessing a temperate climate. In England the plant was called woad, and has been either a spontaneous or cultivated product from time immemorial, and is even now grown for dyers' uses in the Eastern Counties of England. But it requires the heat of a nearly tropical climate to produce the true indigo-yielding plant which contains the colour in such quantity and in such a state of purity or freedom from foreign matters as to make it easy and profitable to extract it. Indigo, under the name of *indicum*, is mentioned by Pliny as in use by artists rather than by dyers at his time. This author believed it was a scum or froth from the sea ; but that it was the same as the modern indigo is evident by his saying that it is to be distinguished from spurious imitations by putting some of it upon live coals, when it burns with a purple smoke. In the middle ages we have tolerably frequent records of blue dyeing by means of woad vats, in which the indigo present in the plant enters into solution by a spontaneous fermentation ; and methods are given in receipt books of the fourteenth and fifteenth centuries of how to collect the foam and froth of these vats, and to make what is called indigo from it for the use of artists, the name being, doubtless, given to it because it resembled and possessed the chief properties of the material already known as indigo. Afterwards woad itself is found to be called indigo in

some places, but this carelessly or inaccurately.* The imported indigo appears to have been known at this time to the Italian and French as *bagadel endigo*, *baccades* or *bandas*, or *indaco del golfo*. Under the name of "inde de Bandas, c'est à dire Baguedel" it is prescribed in a receipt of the year 1410, with what seems to be a deoxidizing mixture, in order to make a blue colour for staining cloth in the manufacture of imitation tapestry.† But the only undoubted ancient receipt in which it can be safely said that indigo is used with deoxidizing agents is to be found in the Bolognese manuscript translated by Merrifield, No. 362, in which lime and honey are the reducing materials, the object being to dye silk a blue ground to be converted into green. The date of this receipt can hardly be later than 1450, but from the mention of indigo in Italian charters and contracts of a much earlier date (1194) it may be surmised that methods of employing it in dyeing were known long before 1450. Some writers having stated that indigo was only known in Europe after it was imported from the East Indies by the Dutch, Bancroft quotes in contradiction the work of Caneparius, which was printed at Venice in 1619, who describes *Endego* as being brought by merchants from India to Alexandria in Egypt, and to Syria, and thence to Venice; and further he states that it is used by dyers, "who dissolve it in vats with a lye of wood ashes and other wares, accord-

* See Merrifield, ii., p. 44, for some very curious processes.

† See Textile Colourist, i., p. 203, from Merrifield, i., p. 85.

ing to their own practices." Concerning which he says "it is not my office to give instruction," which may be either because he did not know the methods, or, knowing, did not feel at liberty to communicate them. This secrecy makes it impossible to satisfactorily trace the dates of the various improvements which took place in the application of indigo, as, for example, when the lime and copperas vat began to be used.

It is not unfrequently stated that Queen Elizabeth prohibited the use of indigo in this country, but it is not exactly so, the edict had reference to the woad plant, which was submitted to fermentation or semi-putrefaction, and caused a nuisance by the vapours it evolved; indigo at that time must have been very little known in England.

The manufacture of indigo from the plant is very simple; a short account of it will show clearly how the various degrees of excellence of different samples of indigo may be accounted for. The plant being cut is put into a cistern with water and pressed down, fermentation soon sets in, and the colouring matter enters into solution in the water, accompanied no doubt by the other soluble or extractive principles of the plant. In twelve hours the liquid is drawn off into a stone cistern, there it is beaten or churned up, so as to expose it to the air, a little oil being added to keep down the froth; the indigo, by the action of the air, falls out of solution, precipitates to the bottom. It is collected, drained to a paste, and dried.*

* See Robley, *Trans. Soc. of Arts*, ii., p. 233. *Textile Colourist*, iii., p. 166.

The description of the process of extracting indigo from the plant given by some writers is very lengthy, and makes it appear as a difficult, complex, and delicate operation; but the above simple process is no doubt essentially all that is wanted to obtain the indigo. It is found, however, as a very general accompaniment to the above method that something is added to the liquor, after beating, to favour the more rapid precipitation of the indigo powder; this something may be either lime, earthy matters, or certain vegetable decoctions alone or mixed with earthy matters; these settle along with the indigo, and are never after separated from it until it comes into the hands of the dyer or the indigo refiner. The quality of the indigo of commerce is therefore liable to variation from different causes, among which may be mentioned the quality of the plant itself, which, besides indigo, contains other matters soluble in the extracting waters, and which precipitate, in greater or lesser quantity, along with the indigo; the mineral matters added ostensibly to help the precipitation of the indigo, but it is believed in many cases they are added really to increase the weight of product obtained; the vegetable extracts added also with the view of precipitating the indigo, these are mostly of an astringent nature, and contain tannin matters which precipitate, along with the indigo, a variety of other vegetable, besides mineral, matters in solution. The skilful or careless management of the extraction will also greatly influence the results, for in warm

climates the other vegetable matters existing with the indigo are very liable to enter into fermentation, which may become destructive to the colouring matter itself, to guard against which, boiling of the indigo paste, and other precautions, not necessary to detail, have to be practised. It does not appear that indigo free from other vegetable matter is capable of entering into fermentation or putrefaction. The best kinds of indigo contain about 60 per cent. of pure colouring matter and 40 per cent. of other substances, low qualities may not contain more than 10 per cent. of colouring matter; the methods of ascertaining the amount of colouring matter are given further on.

Such is the nature of the indigo supplied to the dyer and printer; it is not a pure colouring matter, but in its best and purest state must be looked upon as a mixture of pure indigo with other soluble vegetable matters of the indigo plant.

A characteristic property of indigo, distinguishing it from the great majority of dyestuffs, is that for all practical purposes it is, in its state of blue indigo, quite insoluble, not only in water but in any other known fluid; it is true that to a very slight extent it dissolves in several liquids, but on account of the minute quantity dissolved, no use can be made of such solutions, if, indeed, they can be considered as real solutions where upon cooling or dilution the whole of the colouring matter settles out again. As the discovery of a real solvent for indigo blue would accomplish quite a revolution in the applications of

this colouring matter reference may be made to some statements of chemists with regard to its solubility. Aguiar and Beyer state that aniline can be used as a solvent to obtain pure and crystallized indigotine.* Camille Koechlin has stated that it is soluble in some of the alkaloid salts, as acetate and muriate of morphia;† Wartha states that Venice turpentine, paraffine oils, petroleum, spermaceti, and stearic acid can be used to dissolve indigo and obtain it in the crystalline state.‡ Méhn says that it is soluble in phenic acid and may be obtained in crystals, 500 parts of the acid yielding 2 parts of crystals.§ According to Schützenberger, when finely powdered indigotine is mixed with anhydrous acetic acid and a single drop of concentrated sulphuric acid added, a beautiful dark blue liquid is obtained from which the indigo separates unchanged upon the addition of water, and this, he says, is the only case of solution of indigo from which the indigo can be recovered without having passed through the process of reduction.|| The ordinary glacial acetic acid when heated dissolves indigotine in small quantity with a pure blue colour, but it nearly all deposits on cooling. The action of strong sulphuric acid upon indigo may be here referred to simply to state that though it dissolves it, and the

*Ann. Ch. Pharm., clvii., p. 366. Jour. Ch. Soc., xxiv., p. 268.

†Ch. News, xix., p. 31.

‡Deutsch. Ch. Ges., Berlin, iv., p. 334. Jour. Ch. Soc., xxiv., p. 568.

§Chem. News, xxv., p. 58. Jour. de Ph. et Ch., December, 1871.

||Traité des Matières Colorantes, ii., p. 520.

solution retains the blue colour, the indigo, as indigo, is completely destroyed ; another and quite different colouring matter is produced, from which the original indigo cannot by any known means be recovered.

The solution of indigo for the purposes of dyeing and printing has therefore to be accomplished in a circuitous manner, the object is obtained by the aid of a great variety of materials which act chemically upon the indigo, destroying for the time its blue colour, turning it into a substance which is soluble in alkaline liquids, in which state it gains easy admission into porous fibrous substances, and unites intimately with them, and from which state of temporary decomposition it is easily regenerated into its original blue insoluble state, forming one of the most permanent and valuable of all the colours produced by the dyer's art.

According to Bancroft* the fresh leaves of the indigo plant, when bruised upon calico, so that the cloth may imbibe the expressed juice, communicate a greenish tinge which upon drying becomes blue, and stain it in so permanent a manner that washings with soap and water do not remove the colour, but only make it brighter. It is therefore evident that cloth could be dyed in a very easy manner from the indigo plant, and no doubt the spontaneous fermentation of the plant in water would at the earliest periods have indicated the simplest way of using it for dyeing, and so it has happened that until com-

* Vol. i., p. 170. Edition of 1813.

paratively recent dates the only general way of obtaining a solution of indigo for dyeing purposes was by subjecting it to the action of vegetable matters in a state of fermentation, in contact at the same time with some alkaline substance; even at the present day, perhaps, the most general method of dyeing with indigo, and that in which the greatest amount of this dyestuff is consumed, is by means of slight modifications of the ancient process of fermentation.

Without entering minutely into the chemistry of indigo, or discussing its precise composition and behaviour with various reagents, it is convenient to have an intelligible hypothesis which can be used to explain what takes place during the solution, decolourization, and regeneration of indigo blue in its practical applications. Disregarding for the present the condition in which the elements of the colouring matter may exist in the plant, we may look upon indigo blue as a complex body containing a certain number of atoms of carbon, nitrogen, oxygen, and hydrogen. The current theory is that in the process of dissolving indigo in the vats an additional atom of hydrogen is added to it, and a new body produced which has no colour and which is soluble in alkalis; that when this new substance is exposed to the contact of the oxygen of the air it loses its newly acquired atom of hydrogen, which is taken away by the oxygen, and the original blue indigo is reformed. Having stated this, the generally received hypothesis, and without in the least disputing its probability or

its truth, I shall at once put it aside and adopt the older theory, simply because its language is more familiar to readers, while it expresses even more intelligibly for practical comprehensions, and with as much probability, the various behaviours of chemicals upon indigo blue. Let indigo blue then be considered as composed of a colourless body (which may be called indigo white) soluble in alkalies such as soda, potash, or lime water, which is combined with an atom of oxygen to form the blue; this atom of oxygen is removeable from it by means of a number of substances which have a stronger affinity for oxygen than the indigo white possesses, the indigo blue through their agency is *deoxidized* or *reduced* to indigo white and so remains as long as it is cut off from the presence of fresh oxygen, but the moment it comes into contact with free oxygen, or bodies which easily yield up oxygen, it absorbs the atom of oxygen it had been deprived of and again becomes indigo blue. The successive processes of reduction or deoxidation and revival or oxidation may take place repeatedly and perhaps infinitely upon the same parcel of indigo blue properly treated.

In treating of the applications of indigo blue its uses in printing are first taken, and afterwards its employment in dyeing.

Orpiment Blue—Pencil Blue.—This is probably the oldest of the blues from indigo applied as a printing colour. I have no knowledge of when it originated. In the middle ages a mixture of powdered indigo and

orpiment was commonly used as a green pigment by artists, and considering the impossibility of orpiment having been selected by any process of reasoning at that time as suitable to help in dissolving indigo, it would seem likely to have been the result of accident or haphazard experiments upon the artists' green mixture. The earliest date at which the colour is found in receipts is 1746, in Rhyiner's manuscript,* where it is called English blue, the materials and process being nearly the same as those used at the present day. What the nature of the chemical reaction may be that takes place is obscure, but by simply heating together ground indigo, water, potash, and orpiment a strong solution of indigo can be obtained, which when thickened with gum is capable of being printed. The only way in which this colour has been really successfully used is when applied by a sort of pencil or brush, whence its name of pencil blue. The so-called pencil was a rude brush made by reducing the end of a twig of wood into a fibrous mass, and by means of this the colour was painted on the cloth in certain places, generally within outlines or boundages, and served to give the blue part in a floral design. The pencillers generally were far from having artistic tastes, judging by specimens of their work which remain, and were satisfied to give a hasty and shapeless daub of colour somewhere about the right place in the design. The colour was justly valued for its

* Dollfus-Ausset, ii., p. 128. Bancroft in a note to vol. i., p. 211, concludes that the colour was not known to English printers in 1734.

fastness and permitting further treatment of the cloth for the entry of other colours after its application. The application of the orpiment blue by the ordinary methods of printing with block or roller is attended with so much difficulty and irregularity of results that its use is very much restricted; and it may be said for the better class of prints to have been abandoned after the most strenuous exertions on the part of the printers to include it in their regular list of colours. The difficulty resides in the continual absorption of oxygen by the indigo at the surface of the colour, and its becoming blue and insoluble, consequently not capable of entering into the pores of the cotton and washing off when the goods are passed in water.

In Rhyiner's manuscript, under date 1774, this colour was applied to block printing by having a vessel filled with the colour and a floating sieve cloth of canvass on the top, the supply coming from below to furnish the block. Bancroft* gives an account of device practised by Messrs. Hoyle and Sons so long ago as 1795, for printing this colour by roller, the composition being in a close receptacle above the roller and feeding it by means of small openings made at the bottom, by which it was hoped the colour would be applied before it had time to absorb oxygen. This same house more than fifty years afterwards was again occupied with a new method of applying this old colour—a method

* Vol. i., note to p. 210.

patented by Woodroft June 22nd, 1846—the idea of which was to exclude the contact of the oxygen of the air from the colour while working by surrounding it with some neutral or inert gas which could not exercise an oxidizing influence upon it. The gas chosen was ordinary coal gas, and the printing machine was so boxed in that a continual stream of it played on the colour in the box, on the roller, and even on the piece after printing, so as to give time for the colour to be absorbed before it could oxidize superficially. Very excellent results were obtained; blues of all shades from the deepest could be printed sharp, clear, and of good hue. But as a practical process the invention was a failure, and was soon given up.

The orpiment blue is still sometimes worked just in the ordinary way of printing. In the United States it has been a good deal employed in garancine work. It produces an effect and constitutes a style, but as a blue it is very indifferent, and if it was not in comparatively small quantity compared with the other colours of the design its irregularities of shade would at once condemn it.

Hydrosulphite Blue.—This, which is chronologically the latest of the indigo colours, finds its proper place next to orpiment blue, because it is of the same general character, and contains the indigo in the same state, that is deoxidized and dissolved in alkali, only the deoxidizing agent is different. It is the subject of a patent to Schützenberger and Lalande,

dated December 13th, 1871. In Schützenberger's Treatise upon Colouring Matters, published in 1857, attention is drawn* to an observation made by M. E. Schlumberger upon a curious case in which indigo blue is reduced to indigo white in the presence of an acid liquid, no other instance being known. The reducing solution consists of the product of the action of sulphurous acid upon metallic zinc, which was believed to be a mixture of sulphite and hyposulphite of zinc. Fourteen years afterwards this observation bore fruit in the discovery and application of the powerful reducing action of the so-called hydrosulphite of soda, which is made by acting upon zinc with acid sulphite of soda. The reader will not find any account of hydrosulphurous acid or its salts except in the most recent manuals of chemistry, its composition, properties, and formula being even yet only imperfectly known, and the name itself merely provisional. The best and most detailed account which has been printed upon the hydrosulphite blue process is by M. Gros-Renand;† and to the original or the translation the reader is referred for the whole particulars. Here it is sufficient to give an outline of the method of preparation of the reducing agent and its application to the colour. Hydrosulphite of soda is so unstable that it must be prepared but a short time before being used, and can scarcely become an

* Vol. ii., p. 521.

† Bull de la Soc. Ind. de Rouen, ii., p. 17, translated in Textile Colourist, ii., p. 82; also Farber Zeitung, 1874, p. 212; Moniteur Scientifique, xv., p. 655; Chem. News, xxviii., p. 34.

article of commerce, though the colour itself is or was to be purchased in a state ready for printing. The hydrosulphite is prepared by taking bisulphite of soda at 54° Tw., and letting it dissolve as much zinc as possible in the cold and in closed vessels quite filled with the mixture. To precipitate the zinc, dissolved milk of lime is added to the solution until it is slightly alkaline. It then keeps better than when acid, so that with care it may be kept forty-eight hours without being spoiled. When about to be used the zinc oxide precipitate is separated by filtration and pressure, and a liquor obtained standing at 32° Tw. The colour can be made directly by dissolving ground indigo in a mixture of the neutral hydrosulphite and milk of lime, and thickening with gum; but to get the best colours it is recommended to dissolve the indigo first in the hydrosulphite and lime, precipitate it by acid as white indigo pulp, and after slightly washing drain on a filter until 7 lb. of it contains 2 lb. or represent that quantity of good indigo, the pulp being thickened with gum water keeps pretty well. Before printing it is mixed with a large excess of hydrosulphite and a sufficient quantity of milk of lime, the strength of colours varying from $6\frac{1}{2}$ oz. per gallon for the darkest shade to $2\frac{1}{2}$ oz. for lighter shades. The colours must be worked warm, *i.e.*, between 86° and 95° F., and it is said as many as six or eight pieces can be printed without emptying the box. After the goods have hung for a short time they can be passed in very

weak chrome liquor, well washed, and soaped. I have not had much experience with this colour, merely having tried to work it. As soon as I had prepared some of the colour from the first accounts of it which reached me I recognised in the hydrosulphite the cleanest and most powerful deoxidizing agent which has hitherto been applied to indigo; but having had a good deal of experience with other reducing matters, I saw that the colour was not in the least degree easier to manage than the old orpiment colour, that it could not be made so strong as the orpiment colour, nor yield shades as dark as it, and I felt satisfied after printing a few pieces that it was not the colour which printers have been waiting for, and and that it could only receive a very limited application. It is worked to a small extent on white grounds, where it may be combined with aniline black and alizarine colours. It gives a pleasant shade of indigo blue of medium depth. It does not seem possible to obtain dark blues from it, the darkest colour recommended by Gros-Renand containing only about 7 oz. of indigo per gallon, while an orpiment blue of more than double that strength can be readily prepared.

Oxide of Tin Blue.—An indigo colour of the same class as the two just treated of can be prepared by using the protoxide of tin, or even metallic tin, as the deoxidizing agent, in conjunction with caustic alkalis. This colour is more uncertain than either the orpiment or hydrosulphite blue, and can only be used for

light covers. It is also very expensive, and has consequently fallen into disuse. It is not to be confounded with the fast or precipitated blue also made by means of tin, which is in an insoluble state as printed, and the fixing of which requires a separate operation.

Other deoxidizing agents, such as glucose, have been employed to obtain a solution of the reduced indigo for printing, but these colours have not been found suitable, and have never received general application.

The above cases are all that I know of in which it has been attempted to apply indigo in the reduced and dissolved state. They have not been practically successful, and it still remains for inventors to discover a real solution of indigo which can be applied in calico printing to obtain dark and light blue shades.

China Blue.—This colour was extensively worked in England before the commencement of the present century. It probably originated about the middle of the last century, but there are no means of fixing the date or the place of its discovery. It is not mentioned in Rhyner's manuscript, which comes down to 1783. Persoz speaks of specimens nearly one hundred years old in his time (1846), and refers to some instructions concerning engraving flat plates for it dating 1780. The earliest English patent which mentions this colour is dated February 1st, 1809; it is referred to as a well-known colour, and describes, as new, a process of obtaining a fast green colour from it by using tin in its composition, a sufficient amount of

this metal being left after the dipping to serve as a mordant for dyeing in weld.

The earliest receipts for China blue prescribe only indigo, sulphate of iron, and water thickened with gum. Later on numerous modifications were employed, and addition of iron liquor, orpiment, tin salts, and similar materials, came into use, but it does not appear that anything more than a salt of iron is required, and not even that for light colours, the main point in the preparation of the colour for printing being to have the indigo extremely well ground. For this purpose it was submitted in proper mills to a grinding process for two or three weeks. The longer it was ground the better was the result, the mill preferred being that known as the "cradle," which, from its combined rubbing and rolling motion, was very suitable for the purpose. The colour after printing was fixed by dipping the pieces alternately in vats of lime water and sulphate of iron, the first dip being in the lime vat. The indigo became reduced and dissolved in the places where it was printed, and at once absorbed by the fibre. In the old style of dipping on frames, by which the best class of work was done, the process was slow, one man taking two or three hours to do about 100 yards of print. By a continuous passage of the pieces through alternate lime and iron vats, there was an economy of labour, but some styles could not be done by this process, and the results were subject to irregularity. After the dipping of the pieces, they required to be

cleansed from a thick coating of slime, consisting of sulphate of lime and oxide of iron. This was effected by means of dilute sulphuric acid, followed, if required, by a warm souring and slight soaping. The blue colours thus produced resembled in shade the blue on China ware, whence the name given to the colour. Deep shades could not be obtained; but the dark blue was sufficiently deep for producing effective designs in contrast with the lighter shades. The colour could be worked with a resist and covered, giving rise to a great variety of prints. The colour was fairly fast, though somewhat superficial, and though actually a pigment as applied by the plate or roller, it permitted the use of the most delicate engraving. Changes of taste and the costliness of the colour and fixing have placed this style of print, once very popular, in the background. It is now very seldom seen.

Precipitated Blue—Fast Blue.—This name is given to a colour which, as it is printed, consists essentially of reduced indigo in the insoluble state. The reduced indigo was obtained by precipitation of it from a solution which was most usually prepared by boiling blue indigo, protochloride of tin, and caustic alkali together. Some times the indigo was dissolved by a prolonged boiling of it with feathered tin and alkali. The solution of indigo made by lime and copperas could also be employed. The addition of acid caused the precipitation of the white indigo as a pulpy mass which could be separated from the liquid by filtration. In the state of wet paste this precipitate did not

oxidize very quickly, and in proper vessels it could be kept for several weeks. For use it was mixed with gum water, and some times a small quantity of crystals of tin. The fixing should be effected as soon after printing as possible, and is best done by passing the pieces over head into a tolerably strong alkaline solution, soda ash or lime, or silicate of soda. The alkali makes the white indigo soluble, and it then penetrates the fibre, and becomes fixed there by exposure to air. This colour has only a very limited application in calico printing at present. It was formerly much used for a cover to fancy chintz patterns, being the only tolerably fast blue suited for that style; by itself it is too weak to be satisfactory. This blue is interesting as being the basis of the only tolerably successful attempts to combine indigo colours with dyed colours by one printing which may be noticed in this place.

Combination of Indigo with Dyed Colours.—

Before the application of extract of madder and artificial alizarine and the present extended use of pigment colours, it was a matter of much importance to be able to vary the regular madder and garancine styles by the introduction into the designs of indigo blue, and with it the yellow from chromate of lead, and green from the mixture of these two colours. The two principal attempts in this direction are to be found detailed in Philippi's patent of November 25th, 1840, and in Lightfoot's patent of December 26th, 1867. Philippi's patent is for printing reduced indigo

mixed with tin, alone, or mixed with lead salts, and also with lead salts alone, and these colours along with madder colours or mordants. The pieces after printing were passed through cow dung and ammonia, or carbonate or bicarbonate of soda, or other alkaline carbonate, then through a mixture of bichromate of potash and a carbonate (when lead salts were printed), and the pieces afterwards dyed in madder and cleared. This process was put into work, but after struggling some time with it the proprietors relinquished it as a failure. The only specimens I recollect seeing of this style were five-coloured fancies, on white grounds, resembling the present extract style, but the colours were inferior, and, I was informed, subject to great irregularity. In Lightfoot's patented process the indigo was prepared in precisely the same way as for precipitated blue, and simply thickened with gum water for printing. A green colour was prepared by mixing lead salts with the blue, and a yellow colour from lead salts alone, in this respect not differing from Philippi's patent. The colours were printed along with mordants for garancine dyeing, the pieces slightly aged, and then went on to the fixing. In the fixing Lightfoot used silicate of soda, which, though commonly used for fixing mordants, had perhaps not previously been used to fix reduced indigo in this way. To fix the indigo the silicate was employed at about 8° Tw., and a temperature of about 90° F., the time of contact being from a minute to one-and-a-half minute, the goods passed immediately from this strong

silicate into abundance of cold water, in which the indigo became oxidized, changing from green to blue, then well washed. The next process was to pass the goods through warm bichromate of potash, to develop the yellow and the yellow part of the green, and then after washing might receive a slight dunging, after which they were dyed in garanceux made from spent madder, and cleared as usual. A house with which I was engaged on the Continent having purchased the right to use this process, it was applied there under my direction. Nothing was spared to ensure its success; I had the advantage of the personal instruction of the inventor, who was then managing the Lower House Printworks, near Burnley; but after every exertion made it was practically a failure, and given up. Very good work was produced when everything was right, and there is no doubt that it was the best attempt which had been made to produce indigo colours combined with garancine colours, and there were great hopes that a new and attractive style had been created. The difficulties, however, were considerable, and the risk of producing bad work by trifling negligence or want of care was too great to make the process practicable. In the first place the colour required great care in printing, it was easily injured, and became worse with every piece printed. In order that the indigo might not become oxidized on the cloth the goods printed with black and chocolate mordants had to go into the dye-house with insufficient ageing; the silicate at 8° Tw.

and 90° F. proved very difficult to manage; if too strong or too warm, it dissolved out the alumina of the mordants; if too weak or too cool, it did not fix the indigo; if there was much yellow in the design, or if the garancine mordants were strong, the silicate was quickly decomposed, turning into a jelly from separation of silicic acid, and becoming quite useless. In addition to these difficulties, it was an expensive style, much indigo being lost. Such success as this process met with was mainly due to the use of garanceux as the dyeing material, for owing to the preparation of this substance it was more free from foreign and injurious matters than any other dyestuff of the madder class at that time available, and it left the blue, green, and yellow colours much purer than madder or garancine would leave them, requiring but slight clearing operations to finish the work.*

Ward's Patent Process.—This patent, dated December 8th, 1857, is for a method of applying indigo by printing, and depends upon principles different from those already treated upon. The indigo was in the blue state, finely divided by grinding and digesting with caustic soda, then mixed with pulp of slacked lime and grape sugar or glucose. The latter substance had been long known as an effective reducing agent for indigo. It does not act in the cold, and the point in this patent was to print the indigo along with deoxidizing and dissolving agents which did not come into operation until the

* See *Mechanics' Magazine*, 1869, p. 30, and *Technologiste*, xxx., p. 30.

print was submitted to heat. A very short exposure to steam caused the ingredients of the colour to react upon one another; the indigo was deoxidized, dissolved, and absorbed by the fibre, and afterwards oxidized and fixed by exposure to air or oxidizing agents. This process was applied at two or three works in Lancashire. It was capable of yielding very dark and saturated colours, but it failed to give satisfaction in several respects, and very soon fell out of use.

Underwood's Process.—This was patented December, 6th, 1875, and was an attempt in the same direction as the last. Instead of glucose the inventor uses amorphous or red phosphorous as a suitable deoxidizing agent, which does not act in the cold. He claims also ordinary phosphorous, either in solution or in a finely divided state. The indigo is mixed with caustic soda, pulp of slacked lime, and the phosphorous, and printed; after printing steamed for an hour, then washed in water or passed in weak acids.* I have seen very fair colours done by this process, but it is perhaps too early to say whether it will be found practically available or not.

Other Steam Indigo Colours.—The two last processes are really steam processes for fixing indigo. There have been others proposed which deserve mention. Hartmann on June 19th, 1855, patented a steam indigo blue, made by mixing 10 lb. of precipitated indigo, 1 gallon of gum water, and $1\frac{1}{4}$ lb.

* See abridgment, *Textile Colourist*, ii., p. 163.

of magnesia. To obtain green colours lead salts were mixed with this colour to be afterwards chromed. On September 14th of the same year the same patentee claimed the use of silicate of soda instead of magnesia as the alkaline agent in this colour, and the production of mixed colours by using quercitron bark in conjunction with the indigo. M. E. Schlumberger states that indigo mixed with hydrated oxide of tin and cyanide of potassium, then thickened with gum water, does not become deoxidized until submitted to heat, and can be used as a steam colour; but he states it is not a practical colour, on account of its cost, tendency to run in steaming, and inapplicability with any colours disengaging acid vapours.*

Zürcher states that hydrated oxide of tin, with indigo and bicarbonate of soda, furnish a steam indigo blue, but it requires quite a special kind of steaming in very moist steam. Jeanmaire, in reporting upon Zürcher's process, says that carbonate of potash is preferable to bicarbonate of soda. This chemist states that moisture in the steam is not so important, but that absence of air or oxygen in it is of great importance, and quotes experiments in proof of his opinion.†

None of the processes last mentioned have any practical value, and have never even been extensively tried. They are only noticed here to complete the subject and for what value they may possess as guides or

* Schützenberger, *Traité des Matières Colorantes*, ii., p. 600.

† *Textile Colourist*, i., p. 332, from *Bull. de Mulhouse*, 1876.

warnings to future experimenters. There are no other known methods of applying indigo by printing, and it will have been observed that none of those described in the last few pages are satisfactory, while it may be said that most of them are admitted failures. No colouring matter has been more experimented upon than indigo with the distinct aim of using it for printing. The question proposed seems simple and plain, but the answer has not yet been given. No one has been able to furnish the printer with a solution of indigo which can be used and fixed in a simple and practicable manner. I have no doubt that this unsolved problem, which is the reproach of the art, will some day, and perhaps soon, be resolved in a satisfactory manner, by means either not now thought of or by some happy modification of methods already known. It is true that such a colour now would perhaps not have the value it would have had some ten years ago; but when we consider the complicated, tedious, and expensive processes of producing blue-coloured goods by dipping with resists, or by discharging afterwards, and the great stability and permanent usefulness of indigo blue, which can never go out of fashion entirely, it seems certain that any method would be highly valued which would permit the direct printing of indigo or the printing of some quasi-mordant for it, to produce at one operation the effects now produced by resists and discharges which involve a considerable loss of colouring matter by actual destruction of it.

Indigo Dyeing—The Woad Vat.—Woad, as previously mentioned, was used for blue dyeing in Europe before indigo was known. This plant, put into water, enters into fermentation spontaneously; but it was not generally delivered to the dyers without a previous treatment by the grower, which consisted in grinding or crushing it in a half dried state to a pasty mass, which was allowed to enter into fermentation for a short time, and then by drying the further progress of the fermentation stopped. To prepare it for dyeing it was simply necessary to put it in warm water, when the fermentation recommenced; to prevent it progressing to a destructive extent, lime or solution of wood ashes was added, and the vat was ready for dyeing. If woad be taken as thirty times weaker than the Indian indigo plant,* and this latter as containing in its green state only about one two-hundredth of its weight of indigo, it is evident that the strongest woad vats must be comparatively weak in colouring matter, and incapable of yielding dark colours. The more modern dyers added foreign indigo to strengthen the vats, still looking upon woad as the basis. Thus we may rationally account for the continuance of the use of woad in indigo dyeing, and the name of woad vats and “woading” common in the woollen dyeing districts of England. Mr. Jarman states that only the very old woad vat and the quite modern hydrosulphite

* So several authorities state. Hellot says that indigo is fifty times stronger than pastel, but Chaptel believed it was not so much stronger. (Leuchs.)

vat are used in England for wool dyeing; the latter, however, to only a small extent. This state of affairs can only be looked upon as a fondness for old ways, because on the Continent the use of woad or pastel has been given up for better methods. The setting of a woad vat, as employed at the present day by the Yorkshire wool dyers, is given by Mr. Jarmain as follows:—*

Lincolnshire woad	560 lb.
Bran	18 lb.
Slacked lime (dry)	22 lb.
Madder	2½ lb.
Indigo	24 lb.

These quantities differ in some respects from those given further on by the same author. The amount of woad is large, but in refreshing the vats no more woad is employed, but only indigo, bran, and lime, so that it may happen before a vat is emptied that as much indigo as woad enters into it. From the known composition of fermentation vats used in France and Germany, it may be concluded that the only really essential constituents are indigo, bran, and lime. The use of madder in this kind of vat is very old, but that also is given up by enlightened dyers. The idea that the alizarine contained in so small a proportion of madder as given above could have any influence upon the colour dyed is untenable. In the older vats the quantity of madder used exceeded that of the indigo, and might possibly have an influence upon

* Cantor Lectures, Society of Arts, 1876, Textile Colourist, ii., p. 251.

the shade produced, provided the dyed goods were not washed or soured after dyeing; but the real use of the madder was that it yielded a saccharine principle which helped to sustain the fermentation, and it is now replaced by molasses. Wheaten bran readily enters into fermentation, but it contains only a small proportion of soluble matters which can support a continued fermentation, and the action is soon over, hence the necessity of having a large reserve mass of fermentescible matters in the Yorkshire woad vat, which is found in the woad itself, or the necessity of continually adding some similar matters which may be either madder or molasses, as practised in other kinds of vats in use upon the Continent.* Not to enter into great detail upon the properties of these fermented vats, it may, however, be mentioned, that success depends upon keeping the fermentation within due bounds. If it is allowed to get ahead of the point necessary to bring the indigo into solution, the vat becomes putrid, and indigo is destroyed. Lime is the agent for restraining the fermentation, and bran the agent for promoting it. The dyer has to keep a continual watch upon his vat, so that he may maintain it always in a healthy state. Vats of this kind are always worked warm, and may be run from three months up to two years without clearing out. Besides being used for woollens, they are not unfrequently employed to dye heavy cotton goods

* For several kinds of indigo vats for wool dyeing, see Dumas' *Précis de l'art de la Teinture*, p. 203, and De Vinant in *Textile Colourist*, ii., p. 68.

which are not intended for printing upon afterwards. Warm vats cannot, of course, be used for dyeing goods printed with the ordinary resists. The precise nature of the chemical action which takes place during fermentation can only be conjectured. During the changes in the composition of the vegetable matters which are induced by fermentation, there must be produced deoxidizing bodies which are capable of acting upon the indigo and changing its composition also, but what these bodies are cannot in the present state of chemical knowledge be defined. With regard to the loss of indigo by destruction which accompanies the too advanced state of fermentation, Dr. Schunck has observed that formate and acetate of soda have the property of causing indigo blue to disappear when they are mixed with reducing solutions such as grape sugar and soda, or protoxide of tin and soda. Even by boiling indigo with alcohol and caustic soda mixed with acetate of soda this disappearance takes place, no reducing agent being present. He considers that the occasional disappearance of indigo in the woad vat is to be explained by the formation in the vat of alcohol and acetic acid, and he recommends that the use of materials containing starch or sugar should be avoided.*

Copperas and Lime Indigo Vat.—The earliest mention I find of the employment of the copperas and lime vat, is in Rhyiner's manuscript, where it is

* Manchester Society Proceedings, 1864-5. Journ. Chem. Soc. (2), iv., p. 462. Chemical News, xi., p. 69.

described under the date of 1766,* but he gives no information of how long it had been in use previously, merely remarking that it was preceded in Switzerland by the vat prepared with madder, bran, and potashes, and which was found difficult to manage, preference being at that time given to the copperas and lime vat. This vat, as its name indicates, is composed of indigo, lime, and copperas (sulphate of iron), and its action rests upon the disposition of the protoxide of iron, separated by the lime from the copperas, to pass into the peroxide by absorbing oxygen from the indigo and reducing it to the white soluble state. It is almost the only indigo vat used for dyeing calicoes for printers' purposes. It is worked cold, is easily managed, and economical. The proportion of the copperas to the lime varies considerably in different receipts, and no fixed weights can be given, for though copperas is a salt of very regular composition, and quite soluble in water, the other active element of the vat, lime, is not only irregular in its nature, but from its slight solubility in water, and from different ways of slacking it and using it, no proper estimate can be made of how much of it is in an active and how much in an inactive state. Practically the weight of lime used is somewhat greater than that of the copperas, in the ratio of 3 to 4, 4 to 5, or 8 to 9. These ratios are very different from the indications of theory, for if two equivalents of lime were to be used for one equivalent of copperas, the latter

* Dollfus-Ausset, ii., p. 126.

would be in weight two-and-a-half times greater than the lime, so that in practice a great excess of lime is employed. The proportion of copperas to indigo is subject to the same variations, 1 lb. of copperas to 1 lb. of indigo being the smallest amount used in any receipt which has come under my notice, while in others the weight of copperas is double and treble that of the indigo. The proportion between the solids and the water in the vat vary according as the vat is required to be strong or weak. The preferable method of mixing the materials for this vat is first to dissolve the copperas in the water of the vat, then add the indigo, and lastly the lime. By keeping the mixture in suspension for a few hours, by raking up at regular intervals, the vat may be ready for dyeing in twenty-four hours after setting.* This vat can dye all shades of indigo blue, from the lightest sky blue to the darkest Navy blue; but to obtain dark colours repeated dippings, with alternating exposure to the air, are necessary. For the lighter shades of blue a contact of one or two minutes with the dyeing solution is all that is required. The woad vat (or fermentation vat) and the lime and copperas vat are the only generally used vats for indigo dyeing; but there are many other methods and materials by which indigo can be reduced and dissolved, and some of those now, or formerly in use, may be briefly referred to.

* An excellent detailed account of the management of the copperas and lime vat, as applied to dyeing on an extensive scale, by Mr. G. H. Underwood, is to be found in the *Textile Colourist*, vol. i., p. 63, and following pages.

Various Indigo Vats.—A vat made from lime and tin crystals, instead of copperas, is said to be employed in some cases of silk dyeing, and to yield very pure shades of blue. It is very expensive compared with the copperas vat, and it is difficult to see what advantages it has over it.* The use of finely-divided metallic tin as a deoxidizing agent is suggested in Barlow's patent of August 15th, 1860. Metals generally in a state of very fine division, obtained by means of electricity, distillation, grinding, etc., are patented by Leonhart, December 1st, 1860. Tin and iron are specially mentioned in this patent, but proportions are given for tin only.

The use of metallic zinc in powder is patented by Paraf, on August 1st, 1866. It is stated that 1 or 2 parts of zinc, 2 to 4 parts quick-lime, and 3 to 4 parts indigo, have given good results. The process includes the production and preservation of the reduced indigo in bottles, so that it may be used at any time to strengthen a partially exhausted vat. The zinc vat was put into practical operation, but I believe it has not been found to possess any advantages over the old vats.†

Weweirne's patent of June 20th, 1870, is for the use of indigo vats made from indigo, madder, metallic zinc, protochloride of tin, and slacked lime. The vat was to be worked cold.

* De Vinant, in *Textile Colourist*, iii., p. 191.

† Calvert, in *Chem. News*, xxvi., p. 89, gives Schloesser and Co.'s vat as made with 2,000 gallons water, 20 lb. indigo, 30 lb. iron turnings, 30 lb. zinc in powder, and 35 lb. quick-lime. It was ready for dyeing in twenty-four hours.

The hydrosulphite process of reduction dyeing has also been applied to the formation of vats for dyeing. It is a somewhat costly vat, and has not met with uniform success. Its advantages are said to be certainty and simplicity, as contrasted with the woad vat, with which alone it has been brought into competition.*

The use of pectin for reducing indigo has been introduced by Leuchs, and very strongly recommended by him. The process for a small vat is to take 18 to 20 gallons of weak caustic, add as usual 2 lb. indigo, and 30 lb. to 40 lb. of sliced turnips, suspended in a metallic basket; heat to the boiling point. Complete reduction and solution takes place. The vat, when it has cooled down to a proper temperature, can be used for dyeing. One pound of dried turnip is said to be able to dissolve 1 lb. of indigo. The inventor succeeded in making an extract of turnips by means of high-pressure steam, and obtained a product of which 1 part was sufficient to procure the solution of 4 parts of indigo, either in soda or in lime water. I am not aware that this material has been tried on the large scale. It is, however, a commercial article advertised in Continental journals.†

Vincard gives the composition of an indigo vat formerly in use, in which urine was the liquid used.

* Jarman, Cantor Lectures, 1876; Textile Colourist, ii., p. 255; Schützenberger and Lalande's patent, December 13th, 1871; and Halliday's patent, October 21st, 1873.

† Technologiste, xxvii., p. 128; Chem. News, xiii., p. 146; Bull. Chem. Soc., Paris, 1866, p. 153; Muster Zeitung, 1866, p. 32.

By fermentation or decomposition, assisted by heat, the indigo became deoxidized and dissolved. A cold vat could also be made from urine by using 2 oz. madder to each 1 lb. of indigo. It is stated to have been very simple to make, and certain in its operation.

In Leuchs' treatise on colouring matters, reference is made to a curious method of dyeing wool with powdered indigo, without any reducing agent added, given by Fabviez. The wool in the fleecy or unspun state, is placed in a boiler with water, and for 48 parts of it 1 part of indigo is used, being diffused as evenly as possible in the wool. After being slightly heated a solution of potash at 2° Tw. is poured in, the heat is kept up for a week, and the wool is then found dyed. This old plan was revived and patented by Maistre, May 2nd, 1868. In this process the wool, in quite a raw state, containing the natural grease and yolk, is dyed by immersion in an alkaline solution mixed with indigo, the temperature being kept at 95° to 120° F. In a few hours the wool may be taken out, the liquor expressed, and the fibre spread on the ground to oxidize the indigo. The advantages claimed are that the dyeing process is more healthy than the regular one, the colour more brilliant, and that the straw and vegetable substances present are not dyed. In these two cases of indigo dyeing, either the wool itself, or the non-fibrous matters in it, act as the reducing agents.

Dipped Blue Styles of Prints.—It has been seen

that the great difficulties in applying indigo by printing have prevented its direct application in the production of designs on calico. Attention, therefore, was early turned to the working out of methods by which white and coloured effects could be obtained by means of printing upon the cloth either before or after dyeing in the indigo vat. The earliest method of obtaining a design by means of the indigo vat was effected by stopping the entrance of the dye in certain places by previously depositing upon the cloth melted waxy, fatty, or resinous substances. These substances filled and covered the fibre, wherever applied, in such a way, that the indigo dye could obtain no entrance, and when the cloth was withdrawn from the dye and the wax or similar matter removed by hot water, the parts so protected showed white upon a blue ground. The Hindoos used this method from very remote periods, not only for protecting the parts which were intended to remain white on the cloth, but also to protect other colours printed on it from being injured by the indigo dye. When the European nations began to imitate the Indian prints, they soon improved upon this rude wax resist by the discovery of chemical substances which were much easier to apply in the first instance, and easier to remove after the dyeing was accomplished. These substances are called resists because they resist or prevent the entrance of the colouring matter.

At a considerable interval from the time of the development of the resist process printers became

possessed of an entirely different method of obtaining white effects upon an indigo blue ground. This was the *discharging* process, by means of chromic acid, invented by Thompson about 1826, in which the cloth being first dyed uniformly blue, the indigo was destroyed afterwards wherever the discharging agents were applied, and the white of the calico appeared on a blue ground.

The skill and ingenuity which successive generations of dyers and printers have devoted to the various indigo styles, and the ability shewn in combatting the numerous difficulties inherent to them, are worthy of the highest admiration which can be awarded to any technical pursuit. A minute history of these styles would demonstrate more than anything else the immense amount of application of patience, with scientific and technical knowledge, which has been bestowed upon textile colouring. Such a history cannot be attempted within the limits of this work; I can do little more than enumerate the different fundamental processes employed, with references to works where more detailed information may be obtained.

Blue and White—Resist Method.—The white, by resisting, is obtained by printing on a resist paste, which differs in its composition as the shade of blue required is light or dark, which is nearly equivalent to saying as the dyed piece will be a shorter or longer time in the dyeing vat. For light or azure blue the resist may be composed of sulphate of zinc, nitrate of

copper with soap, thickened with gum water. For dark blues, a stronger resist, containing copper salts and sulphate of lead in considerable proportion, must be employed. These resists are partly physical, and are for printing by roller. When printing is done by block, pipeclay is largely employed as an excellent physical resist; but from the presence of gritty matter it cannot be well used in roller printing. The nature of these resists and the dyeing afterwards make it practically impossible to obtain designs in which points or fine lines are necessary for the effect desired. The whites obtained by resisting are defective in neatness and smoothness of outline when compared with general roller printing, and are therefore only used where somewhat massive effects are to be obtained, or where a trail, for example, may be somewhat irregular and thick without injury to the design.

Discharge White on Blue.—For obtaining clear and well-defined whites upon a blue ground, it is necessary to use the discharging process. The discharging colour being a simple solution, properly thickened, can be printed just as any ordinary colour, and with fine engravings; but still it requires very much care to obtain sharp and neat results. The discharging agents most commonly used are chromate of potash on the one hand and a strong acid on the other. They must be applied separately, and the process is capable of variation. The blue-dyed cloth may be padded in chromate of potash and dried, and

the strongly acid solution printed on, oxalic acid being usually preferred. The process may be reversed, or again a colour made with chromate of potash may be printed upon the blue-dyed calico, and the acid afterwards applied by padding or passing the cloth through it.

On February 1st, 1847, Mercer communicated to the Chemical Society the discovery of entirely new materials for discharging indigo blue. These were the red prussiate of potash and either of the alkalies—potash, soda, or ammonia. The salt and alkali could be applied mixed together, or they could be applied successively. The prussiate process has not hitherto proved so commercially applicable as the bichromate process; it is more costly, and more difficult to manage. Attempts have been made lately to employ the prussiate along with milder alkalies, such as the bicarbonates of potash and soda, or with lime water or magnesia, and obtain the discharge by steaming. How far working in this direction is likely to prove successful and replace the chromate of potash processes it is perhaps too early to offer an opinion. Other less practised methods of discharging have obtained for a time, but abandoned in favour of the preceding. Chlorines, hypochlorites, and chlorates have been proposed, and manganese also has been used along with acids.*

* See an article by Depierre, *Textile Colourist*, iii., p. 217; also iv., p. 19. The use of magnesia along with red prussiate for steam discharge was described many years ago, and is referred to in the Author's *Chemistry of Calico Printing*, etc., 1860, p. 145.

Pigment Coloured Discharges on Indigo Blue.—

It will be seen afterwards that there are methods by which certain coloured effects can be produced on blue calico at the same time as the indigo is discharged; but it seems proper to introduce here a notice of a very recent method of printing pigments on indigo blue cloth at the same time as the discharge, producing not white but coloured figures on a blue ground. The idea is owing to M. Camille Koechlin, well known for his ingenuity and chemical skill, as well as for his profound knowledge of printing and dyeing. The discharging agents in M. Koechlin's process are chromate of potash and acids, as in one of the cases given above. Albumen is the vehicle to hold on the pigment, and the pigment may be any coloured body which can be printed and withstand the action of the rather strong acid treatment necessary. Neutral chromate of potash is dissolved in albumen water, and the pigment added, the mixture printed, dried, and "cut" by acid; the albumen partly coagulated by drying is so far further coagulated by the action of the acid that it fixes the pigment mixed with it, and does not prevent the oxidation and destruction of the indigo by the liberated chromic acid. The number of pigments applicable on this style is very limited; almost the only ones used are vermilion and chromate of lead, and the latter is difficult to manage. The coagulation of the albumen is not of the same perfect nature as that which takes place by steaming, and the pigments are not so securely united to the fibre.

M. Jos. Depierre has invented a modification of this style by employing the red prussiate and alkali discharge referred to above. He finds that red prussiate dissolves largely in albumen water without injuring it. By adding bicarbonate of soda and suitable pigments, printing, and steaming, coloured discharges are obtained. M. Horace Koechlin objects that this method is not applicable to dark blues; but M. Richard states that if the blue calico be padded in red prussiate, and then printed upon by albumen water containing pigments and magnesia, successful results are obtained. Lime water thickened is sufficient to give a white discharge.* If this process should turn out really practical, it will be possible to widely extend the range of pigments which may be brought into use.

Coloured Resists—Blue and Orange Style.—

This once very important and still extensively worked style is said to have been first introduced by Koechlin Brothers, of Mulhouse, in 1820. It is mostly connected with the name of Walter Crum, according to Persoz, because he contributed most largely to its perfection.† It is produced by printing a resist containing sufficient lead to form the basis of a chrome orange. The lead is for the most part in the state of

* This style only appeared in 1876. See *Textile Colourist*, iii., p. 217, 288; iv., p. 19; *Bull. de la Soc. Ind. de Rouen*, v., p. 121.

† *Bull. de Mulh.*, xli., pp. 227, 237; a formal claim signed by several printers in favour of D. Koechlin's various discoveries. *Persoz*, iv., p. 318. In my manuscript notes I find concerning the collection of designs preserved in Peel Park, Salford, Manchester, which extends from 1767, that under the date 1817 there are indigo styles with chrome orange and yellow.

insoluble sulphate, which becomes partially decomposed and fixed by the lime in the indigo vat or by a separate preliminary dipping in a lime vat. After the blue has been dipped to the required shade, the cloth is immediately put into dilute sulphuric acid, by which the oxide of lead set free from either the sulphate or soluble salts of lead by the lime is converted into sulphate, which, by treatment with boiling chromate of potash and lime, is converted into the orange chromate of lead.* If yellow, not orange, is wanted, chromate of potash without lime is employed; or the orange after raising is brought back to yellow by acids.

From the methods above given, properly combined, a considerable number of styles may be produced. For example, the two-blue style, which is a light blue figure upon a dark blue ground, is obtained by first dyeing calico uniformly light blue and then printing the figure or design with resist and dyeing up to a dark shade; the resist preserves the light blue from receiving any further colour. Blue, orange, and white differs from blue and orange only by containing a simple white resist in addition. By printing an acid or an acid salt upon the chrome orange, it can be changed into yellow or into white. Green effects can be obtained by dyeing blue over a chrome orange and after treatment with acid, or by printing on a resist largely composed of lead salts and Prussian blue, and

* For details of this and several other indigo styles, consult Underwood's papers in the first volume of the *Textile Colourist*, 1876.

chroming after dipping. The discharging power of chromic acid may be utilised in the two-blue and white style, where white and orange resist is printed on light blue, the orange raised in chrome, and afterwards the blue, under the orange as well as the orange itself, destroyed by passing the goods through pretty strong acid, leaving only a white. These and many other variations are readily produced.

The Neutral or Lapis Style.—Without entering into the styles which may be produced by blocking colours into white parts resisted by the ordinary resists, passing reference may be made to what was called in England the neutral style, and abroad the lapis style (from lapis-lazuli). This style probably originated and was developed in a rude way in India, but it was carried to great perfection in England at the beginning of this century, and formed the highest and most expensive class of prints then produced; it passed over to Mulhouse in 1808, and several houses there engaged in the production of this style. It was in vogue for many years, but is now hardly ever seen in these countries, being very expensive to produce, and only effective where large masses of colour are tolerated in designs, producing a rich but somewhat bizarre effect. The cloth was printed with a *neutral* resist (whence the name of the style) for the white, with ordinary madder black mordant for blacks, with a resist red mordant for reds, and in later days of this style with a resist catechu. Except the black, all the colours were resist colours, the red being made

resistant by means of pipeclay and chloride of zinc (with bichloride of mercury in block printing) and a free use of fatty matters. The colours being printed, the cloth was dipped in a strong indigo vat, when all the parts not printed upon were dyed of a somewhat full azure blue. The vats were required to be so strong that the shade of colour required should be dyed in from three to five minutes, for a longer time in the alkaline liquid would be injurious to the reds. The blue being dyed, the pieces were well washed and dunged, then dyed in madder and cleared in bran. The colours now on the piece would be black, red, blue, and white. In nearly all the designs of this style the full effect depended upon blocking yellow upon these colours, which on the best class of work was done by printing an alumina mordant, ageing, washing, and dyeing in quercitron bark. The yellow falling on the blue in places, gave a green, and on the red in parts an orange, so that there would be seven or eight colours in the print, all good and fast. I had experience in working this style in Russia, where it still lingers, but is done very well by some houses, and can well understand the enthusiasm with which I have heard very old English printers speak of this style as it was worked in England fifty years ago or more; for though there is much labour and trouble involved in it, and it comes round slowly, yet when it is well done it is highly satisfactory, and seems to have been worth all the trouble and cost spent upon it, at least in the eyes of the colourist.*

* Pretty full details upon this style may be found in Persoz, vol. iv.

Besides the styles which have been glanced at, indigo has been the basis of many others, such as Warwick's green, the plumbate of lead green, etc.; but they are almost all gone out of use, partly because the high price of indigo has operated against them, and partly because more attractive though less solid colours have displaced them. The chief characteristic of indigo as a colour upon textiles is its solidity or fastness. It is not a bright colour, nor does it seem possible by any treatments which have yet been devised to heighten or improve in the slightest degree its natural shade as deposited upon calico from the lime and copperas vat, hence it must always be confined to those styles in which durability is of more importance than brilliance.

Indigo and Sulphuric Acid.—The action of sulphuric acid upon indigo by which it is made soluble without destruction of its colour, would appear to have been known to chemists at a remote period. Bancroft states that it was not applied to dyeing until 1740, when Barth, of Grossenhagen in Saxony, made use of it, whence it is frequently called Saxony blue. It was soon afterwards introduced into England, for I find in a patent dated August 8th, 1748, the method of making and applying the solution of indigo in sulphuric acid for blue and green colours which are called Saxon green and blue; besides oil of vitriol the patentees use red arsenic, cobalt, and "bole armoniack" in the preparation of the indigo. The so-called sulphate of indigo, or extract of indigo, is largely

employed in wool and silk dyeing and printing; it has few applications upon cotton goods, and those only in low class, loose colours. It is made by the action of the strongest sulphuric acid upon indigo, weak acid having no action upon this colouring matter. Chemists distinguish two or perhaps three different bodies produced by the action of sulphuric acid upon indigo, but the ultimate and complete result with sufficient acid and sufficient time is the sulpho-indigotic acid, which shews upon analysis equal atoms of indigo and sulphuric acid. The compound, however, is not a sulphate of the colouring matter as represented in ordinary language, but a union of the elements of the acid and the indigo in which the characters of both are profoundly changed, and from which the indigo cannot be again separated in its primitive state, retaining in its new state none of its properties except the colour. The sulphate, or extract of indigo, may therefore be looked upon as a true artificial colouring matter, in its dyeing properties having much analogy with the artificial aniline colours, and no resemblance whatever to ordinary indigo. For cotton it has no affinity; it dyes wool and silk without mordant, the resulting dye is but a loose, fugitive colour, fading in the air and light, and completely removed by soap and alkalies. It is seldom used alone in printing or dyeing, but it is found suitable as a blue part for many of the compound colours such as greens, olives, and chocolates. In woollen dyeing it frequently replaces the blue which should

be given by the indigo vat, producing colours of inferior stability. In the preparation of the extract of indigo it is necessary to use an enormous excess of sulphuric acid—ten or twenty times more than is actually required by the indigo, hence some extracts sent into the market are very acid, which is not injurious for several applications in dyeing; but for printing there is sold what is called mild or neutral extract, obtained by dissolving the acid extract and precipitating it by the addition of neutral or alkaline salts such as common salt, carbonate of soda, or acetate of soda, for it is a curious property of the sulpho-indigotic acid that though soluble in pure water it is precipitated from it by the addition of many soluble salts, leaving the excess of acid in the liquor. A preparation called acetate of indigo suitable for wool and delaine printing is made by adding acetate of lead to the acid extract of indigo; there is no real acetate of indigo known, the substance so-called being merely a solution of sulpho-indigotic acid in acetic acid, and it might be more safely and economically prepared by directly dissolving a well prepared neutral extract in acetic acid.

The quality of the commercial sulphate of indigo varies very greatly. Some kinds are found much better fitted for certain purposes than others, and though the choice of the primary materials has much to do with the quality of the product, no doubt the process of manufacture also greatly influences the result. It has been assumed that the commercial

extract is really sulpho-indigotic acid, but there are some preparations which contain a greater or less quantity of a compound containing a smaller proportion of the elements of sulphuric acid, called sulpho-purpuric or sulpho-phenicic acid, which gives more purple or redder shades in dyeing.*

Testing and Valuation of Indigo.—Although chemists and colourists have given much labour to the discovery and perfection of methods of testing indigo, I am afraid it must be confessed that after all there is actually no reliable process on the small scale by which the percentage of real colouring matter in any given sample of indigo can be ascertained with exactness, or say within 5 per cent. of truth. It is true that many processes pretend to give figures with decimals, but no one buys indigo by such tests, simply because the practical results in the dyehouse do not often correspond with the indications of analysis, and purchasers prefer to judge by the external characters of the indigo, or to accept the brand of some well-known makers. A brief notice only will be given of the various proposed processes for valuing indigo in the laboratory.

The most reliable process would seem to be that of treating the indigo so as to make a dyeing solution of

* For detailed description of a modern process of manufacturing extract of indigo, see Max Roesler, *Textile Colourist*, i., p. 269; Dingler, *Poly. Journ.*, *Moniteur Scientifique* (3), vi., p. 394. See also Kletinski, *Technologiste*, xxvii., p. 530; Haefly, *Chem. Gaz.*, xii., p. 79; *Technologiste*, xxiii., p. 38; Boilley, *Chem. News*, ii., p. 321; and Crum's original paper, *Ann. of Phil.*, 1823, vol. xxi., p. 81.

it, and then ascertaining the depth and quality of colour it would dye. A small vat may be made in imitation of the regular vats, say with lime and copperas, or the indigo may be dissolved in sulphuric acid, and its dyeing powers tried on wool. In practice it is found that both of these methods are defective; they are not only long and tedious, but inexact. The lime and copperas vat, however, permits the separation of the indigo and its being weighed, and this has been the favourite method of testing indigo; for though requiring much time, great care, and skill, it was believed to be reliable. But even in the most practised hands it is difficult to get concordant results from two or three analyses of the same sample, and it is never known whether the same proportion of lime, copperas, and water will act equally upon another sample of different strength. It has been assumed that the precipitated indigo from the clear solution is pure indigo after washing from soluble salts, lime, etc. But my experience shews that it very seldom indeed is pure indigo blue, and may contain 16 to 20 per cent. of reddish purple matters, soluble in glacial acetic acid. If the precipitated indigo be dried and boiled with glacial acetic acid, and if it yields a pale pure sky blue solution, it may be considered as really indigo blue; but if it yields a purplish coloured dark solution, it is certainly not all indigo blue. The acetic acid solution may appear blue while hot in the case of a very impure indigo, but upon cooling nearly all the blue

deposits, and leaves a wine red coloured solution, and this is so general that it may be doubted if there ever was a correct analysis made this way, or if ever any one has seen pure precipitated indigo blue from such an indigo solution. If this reddish resinous matter which dissolves with the pure indigo blue was a dyestuff fixing like indigo blue, it might be called indigo purple, and might perhaps be as valuable as indigo blue, but it is something quite different. If it does deposit upon the fibre in dyeing, it easily washes off, for upon boiling in glacial acetic acid cotton cloth which has been dyed with such a specimen of indigo, nothing but a pure blue is dissolved out, having the same colour as if crystallized and sublimed indigotine had been boiled in the acid, the reddish part evidently not having fixed. This alone must be considered as sufficient condemnation of the reduction method, which can hardly give even comparative results.

The action of bleaching agents upon sulphuric acid solution of indigo has been in use for a long time as a means of testing the value of this dyestuff. It was introduced by Decroiselles, and worked upon by Dalton, Berthollet, and Gay Lussac; the decolouring agent used by them being solution of common bleaching powder. The process was modified by M. H. Schlumberger, who made some extraordinary mistakes in his determinations, representing samples of indigo as containing 80 to 96 per cent. of pure indigo.* Later

* See Persoz, i., p. 440, from Bull. de Mullh., xv., p. 277; Chem. Gaz., i., p. 273.

on the bleaching powder solution was replaced by more permanent oxidizing agents, as bichromate of potash, chlorate of potash, and permanganate of potash. Of many modifications of the method of testing proposed, I consider that of Mc.Kinlay by far the most satisfactory.* He takes 10 grains of indigo, and mixing it with $\frac{1}{4}$ oz. of fuming sulphuric acid, leaves them together for sixteen hours, then makes up the volume to half a pint with water, and adds 50 to 60 grains of oxalic acid to the solution; a standard solution of bichromate of potash is then dropped in from a graduated burette until the blue colour is destroyed. He says that 6 grains of bichromate of potash are capable of decolourizing 10 grains of pure indigo. In comparing this process with others in which the solution of indigo is mixed with hydrochloric acid and the bichromate added to the boiling solution, it is found that the point of completion of the reaction is more easily seen, and, what is curious, less bichromate is required. This Mr. Mc.Kinlay had observed especially with poor qualities of indigo. How the oxalic acid in the cold should so act is a subject worthy of investigation. Schützenberger, in speaking of the use of bichromate of potash with the boiling hydrochloric acid solution, says that 7.56 grains of bichromate of potash are required to destroy 10 grains of indigo. This is the theoretical quantity required to convert indigo into isatin, or sulpho-indigotic acid into sulpho-isatic acid; but by using

* See his paper in Chem. News, viii., p. 234.

oxalic acid and testing in the cold it will be found that considerably less than this quantity of bichromate of potash suffices to destroy the colour of 10 grains of sublimed indigotine. Mc.Kinlay's estimate of 6 grains is too low according to my experiments, which point to 6.4 grains as being nearly the equivalent quantity. Though perfectly concordant results can be obtained from this process when operating upon high class indigo, it becomes surrounded with difficulty and uncertainty when testing medium and low qualities, owing to the action of the sulphuric acid upon impurities in the indigo, which sometimes produces bodies interfering with the results to the extent of several per cents. These bodies can sometimes be removed by filtration, but not always, and introduce a fatal defect in all the sulphuric acid processes, which can only be looked upon as approximative valuations.*

Leuchs found that, with few exceptions, the specific gravity of a sample of indigo was in relation to its goodness, the best being lightest, as for example indigo of sp. gr. 1.330 contained 56.5 per cent. real

* For Reinsch's colour test, see Chem. Gaz., vii., p. 453. Bolley's method with chlorate of potash will be found in Chem. Gaz., viii., p. 443; and in Liebig's Annalen for 1850. Wittstein's reduction process, Pharm. Journ., March, 1853; and Chem. Gaz., ii., p. 136. Leuchs' reduction process, Chem. News, xix., p. 250, from Zeitschrift für Chemie, No. 5, 1869. Ullgren's process, Technologiste, xxvii., p. 358; Journ. Chem. Soc., xviii., p. 217. Dalton, in Manchester Memoirs, N. S., iv., p. 437; and Ann. of Phil., xxvi., p. 73. Taylor's method of obtaining sublimed indigotine, not quantitative, Chem. Gaz., i., p. 115; Crum's method, Ann. of Phil., xxi., p. 81. Fritzsche's method, St. Petersburg. Acad. Bull., i., p. 97; and Chem. Gaz., i., p. 201.

indigo; a sample containing 27 per cent. had sp. gr. 1.575, about forty other samples of intermediate value shewing an intermediate specific gravity with some irregularities.*

Patents referring to Indigo.—I proceed to give a number of various unclassified processes and treatments of indigo which have been thought worthy of patenting, excluding those patents which have already come under consideration. For printing deoxidized indigo, Bury has a patent November 3rd, 1838, for transferring deoxidized indigo to air-tight vessels and connecting them with the colour-box; also for the application of cushions and other packings with pressure on the roller for the purpose of excluding the air. Watson, November 8th, 1838, patented the preparation of sulphate of indigo from refined indigo, and the addition of alumina to prepared sulphate of indigo to improve it for certain uses. For continuous dyeing of navy blues, Leese has a patent March 26th, 1839, for an apparatus consisting of a frame in and above the vat, and so threaded that the face of the cloth with the resists on does not come into contact with the rollers. The same inventor patented, November 26th, 1839, a modification of the discharging process by oxalic acid and bichromate of potash; the printed piece was to be intensely heated by means of a stove after it had passed through the oxalic solution. Martin has a process for preparing cloth for dyeing, December 6th, 1854; the cloth is first passed in solu-

* *Technologiste*, xxxii., p. 385, from *Jour. für Prakt. Ch.*, iv., p. 349.

tion of salt of manganese, then in an alkaline solution of orpiment, washed, dried, and then dipped in a hot ash vat; after dyeing the piece was passed in oxalic acid to dissolve out the manganese. For the recovery of copper from pieces printed with resist by treating the cloth with acid and causing the acid to pass over iron or zinc, see Leese's patent of January 26th, 1855.* The same patentee, on May 28th, 1855, patented a process for obtaining indigo from blue rags by means of sulphate of iron or other reducing agents and alkali. Boilley Brothers' patent for making sulphate of indigo is dated March 24th, 1860; the indigo is directed to be fused with bisulphate of soda to prepare a purple blue sulphate; anhydrous phosphoric acid, is to be mixed with sulphuric acid to treat the indigo; vapours of anhydrous sulphuric acid are to be passed over indigo; and indigo treated with chloride of potassium in mixture with anhydrous sulphuric acid, all with the intention of producing an extract of indigo giving a purple blue. Weweirne attempted to patent, September 29th, 1865, the process of topping a logwood bottom with indigo, and claims credit for thus reversing the old system. An apparatus for hooking or stretching goods to be dyed in indigo was patented by Dufrené, November 29th, 1865. This apparatus is of the nature of the *champagne* dipping frame in general use on the Continent. The vats and dipping frames in England are rectangular, but elsewhere the vats are circular wooden vessels, and the

* Details are given in Underwood's paper in the *Textile Colourist*, 1., p. 145.

dipping frames are circular or rather octagonal, the cloth being hooked on to the hooks on radiating arms in regular convolutions. For some improvements in apparatus for indigo blue dyeing which cannot be well described without drawings, the patents of Woodcock and Coulter, November 1st, 1870, and Oldroyd and others, December 8th, 1870, may be consulted. Olpherts has two patents dated May 22nd, and June 10th, 1871, referring to the pressing of indigo in the process of manufacture. Sawyer, November 15th, 1871, patented a process for restoring spent indigo so as to enable it to be used or utilized to advantage. Scald's patent, June 6th, 1872, for improvements in dyeing when indigo is used is simply a process to use indigo only for topping, the bottom being given with cheap or loose dyes, such as annatto, archil, cudbear, etc. Smith's patent of June 15th, 1872, refers to methods of extracting indigo from the plant by means of dilute alkali. Clark's patent of April 29th, 1873, claims muriate of tin and caustic soda as deoxidizing materials to be applied to indigo for dyeing purposes. Lord, on July 25th, 1873, patents new machinery for grinding and pulverizing indigo, a sort of grooved dish revolving with adaptable rollers. Dentith's patent, October 23rd, 1873, for improvements in producing or preparing indigo blue, claims the use of a number of known and regularly used reducing agents, and in addition sulphurous acid. Auchinvoles' patent, July 31st, 1875, is for the recovery of the surplus indigo from textiles, or from water in which they have

been rinsed, by adding carbonate of soda and then hydrochloric acid, when it is said the greater portion of the indigo is carried up to the surface by the liberated carbonic acid, and may be skimmed off. Firth's patent of February 17th, 1876, is for an apparatus of rollers to be fixed to the dyevat by which one or more pieces can be passed through at once at a regulated speed and dye with uniformity. Improvements in apparatus for wool dyeing dispensing with nets and bags are described in Croysdale's patent, October 28th, 1876; for dyeing hosiery goods in indigo vats, Ashwell's patent of November 29th, 1876, describes the use of a perforated cage to contain the articles to be dyed.*

Many interesting scientific and theoretical, as well as some practical points concerning indigo, I am obliged to leave unnoticed, as not coming within the scope of this work, or as requiring more space than their probable practical applications would justify in giving to their consideration; full references to sources of information in other books will, however, be found in the proper place.

Other Blue Colouring Matters.—There is no other colouring matter at all resembling indigo; it stands alone, and without a rival. Two or three other vegetable substances are mentioned as capable of yielding a blue dye, as the *polygonium tinctorium* and *randia aculeata*, or indigo berry of Jamaica;

* For the four last patents, see *Textile Colourist*, i., p. 397; iii., p. 42; iv., pp. 28, 85.

but they are either very little known or have not been found practically useful. According to Metcalf's patent, November 21st, 1844, the leaves of the chicory plant can be made to yield a blue colour when treated in the same way as woad. The other blue matters at the disposal of the colourist are the aniline blues (which do not come under consideration here), Prussian blue, and ultramarine blue.

Prussian Blue.—This colour is said to have been accidentally discovered by Diesbach, a Berlin chemist, in 1710. It may, therefore, be considered as the earliest of the artificial colouring matters. Its preparation was made known in England in 1724.* For many years it was only used as a pigment by artists and painters. The French chemists Macquer, Pileur d'Alpigny, Berthollet, and others, towards the close of the last century, made strenuous efforts to apply it as a dyeing material upon wool and other tissues, but with very little success, owing to a want of knowledge of its properties. Bancroft† gives detailed accounts of the trials made, which are curious and interesting; but it would seem that Berthollet did eventually master the question so far as dyeing silk and cotton was concerned. Previously to this the calico printers had made use of Prussian blue, for in Hausmann's manuscripts, printed by Dollfus-Ausset, and which date about 1780, there is a receipt for Prussian blue on calico, resembling the spirit blue

* See Bancroft, ii., p. 60

† Vol. ii., p. 70.

of more recent times, in which the Prussian blue is dissolved in hydrochloric acid along with acetate of alumina, and thickened with starch. In the same collection there is a receipt for an alkaline prussiate liquor to be made by treating Prussian blue with caustic potash, but what it was used for does not appear. In those days Prussian blue was the source of prussiate of potash, not as now a product of it, and the difficulties of the earlier experimenters no doubt in great measure arose from the excess alkali in the prussiate liquor. It was the chemist Raymond, of Lyons, who, in 1811, accomplished the practical dyeing of Prussian blue upon wool, and perfected it upon other textiles. The proper steam Prussian blue of the calico printers does not make its appearance until about 1828 or 1829, and I do not know to whom the credit belongs of introducing tin salts into this colour in the shape of the prussiate of tin or tin pulp, without which the best blues cannot be obtained. The chief methods of obtaining Prussian blue upon fibres are as follows:—

(1) The simplest blue is that in which ready formed Prussian blue is partially dissolved by triturating with oxymuriate of tin, thickened, and printed. It is what is called a spirit colour, and used only in the lowest class of work.

(2) Blue designs are sometimes obtained by printing an iron mordant, fixing, and dyeing in prussiate of potash acidulated with sulphuric acid.

(3) Light blues upon calico and medium and dark

blues upon silk are obtained by mordanting in a persalt of iron, washing, and dyeing in an acidulated bath of prussiate of potash. One treatment of this kind gives only a pale shade, but by repetition dark colours can be dyed. It has been found beneficial to have a certain proportion of tin salt along with the iron mordant, which prevents the blue assuming a greenish hue, and turns it rather to a desirable purplish shade.

(4) Blues for printing upon calico, woollen, and delaine are mixtures of yellow prussiate (sometimes a small quantity of red prussiate is added) with tartaric acid, oxalic acid, salammoniac, and prussiate of tin. The Prussian blue is formed from these materials without the use of any iron extraneous to them, and results from the decomposition of a portion of the ferrocyanic acid of the prussiate employed, a decomposition which is effected by the excess of acid employed and the heat to which the colour is subjected in steaming.

(5) Dark blues are dyed upon woollen goods by a process similar in its principles to the last given, no iron salts are used, but only the prussiates with acids and salts of tin as the essential ingredients, to which may be added salammoniac and alum. By a protracted boiling of woollen stuff in such a mixture the blue colour becomes developed and fixed. The finest so-called royal blues are thus obtained on merinos and similar goods. To obtain a denser shade it is not unusual to top these blues by a subsequent dyeing with logwood, alum, and tin salts.

The dark Prussian blue upon calico and delaine was formerly a colour of much more importance than it is at the present time ; much labour and ingenuity was spent upon it, and many variations introduced in the preparation and treatment of the chemicals and materials used, but it scarcely calls for a detailed notice in this work, since its application is well understood and presents few difficulties to a practical man.

The chief characters of Prussian blue as a colour is that it resists acid treatments and also exposure to air very well, but is quickly destroyed by alkaline treatments. There is a striking difference in the power of certain Prussian blues as compared with others to resist the action of alkalies, but all varieties yield more or less quickly, losing their blue colour entirely and leaving only a pale buff shade from the oxide of iron. Hence the Prussian blue cannot be called a fast colour, for it is injured by washing with soap or soda, and therefore behaves quite differently to indigo blue. This property of alkalies to discharge the blue has been applied in calico and silk printing to produce white and buff discharge effects upon a blue ground by simply printing upon the dyed blue cloth a thickened mixture of caustic alkali and water. According to Guillouet, a considerable saving of the prussiates may be effected in woollen dyeing by adding a quantity of perchloride of iron along with the tin, the wool acquires at first a green colour, but by boiling and adding a full proportion of acid, it

becomes blue.* An observation of Arnaudon that in the presence of oxalate of ammonia, salts of iron do not give a precipitate with prussiates until an acid has been added is of some interest, attempts have been made to utilise this property of the oxalate of ammonia in dyeing, but I believe without success.

Havraneck found that chrome alum could be mixed with the ordinary steam Prussian blue, producing a peculiar dark green colour, which differs in its properties from ordinary steam green, chiefly by not being changed under the influence of chlorine. The proportions as given by Schützenberger are, red prussiate 1 part, yellow prussiate 4, chrome alum 2, tin pulp 9, tartaric acid 1, starch paste 24.

Dale and Paraf patented a modification of Havraneck's green, May 24th, 1865; they say prussiate of ammonia is to be preferred to prussiate of potash. This salt is prepared by decomposing the prussiate of potash with hydrofluosilic acid, removing the precipitate and neutralizing with ammonia, or they use chloride of ammonium with the chrome alum. Proportions prescribed in this patent are 40 parts yellow prussiate (or 30 parts prussiate of ammonia) with 8 parts chrome alum, this gives a very fast shade of colour. By using chloride or nitrate of chromium brighter colours are obtained, but not so fast; sometimes prussiate of tin is to be employed.

Ultramarine Blue.—This pigment being delivered

*Schweiz Gewerbeblatte, ii., p. 119; Muster Zeitung, 1854, No. 3. Chem. Gaz., x., p. 414.

to the printer ready formed, has only to be mixed with the vehicle chosen for it, either albumen or lactarine, printed and fixed by steaming, or as sometimes done by passing the goods into boiling water. The history and manufacture of this pigment though full of interest, do not properly belong to this work; being an insoluble powder it cannot be employed in the way of dyeing, but it finds a large consumption in bluing goods for finishing, a sufficient quantity of it being taken up and retained mechanically by the fibre to produce the desired effect.

Blue pigments from cobalt and molybdenum have been manufactured but have not yet come into use for calico printing.

Logwood.—Logwood is very seldom considered as a blue colouring matter in formal treatises,* but its familiar name in several European languages is *blue wood*, and a consideration of the colours it yields both alone and in combinations confirms the correctness of the popular name. It yields blue colours very much resembling indigo in appearance when employed in a sufficiently small proportion upon the principal textiles. These blue colours are so calculated to deceive the buyer, and are so wretchedly inferior in stability to indigo that it is easy to conceive why, as a result of general complaints soon after its introduction into

* Schützenberger places it between Brazil wood and Sandal wood; in Calvert's work, edited by Stenhouse and Groves, it is called a red wood (p. 113), and so in other works, although under no circumstances whatever does it give red colours.

England, its use by dyers was strictly prohibited, and its destruction wherever found, ordered by law passed in the 23rd year of Elizabeth. This enactment remained in force for nearly one hundred years; and though this dyestuff was illicitly used, the prohibition was a great grievance to the dyers generally who obtained the repeal of the statute in the reign of Charles II, the ostensible reason for the repeal being that such improvements had been made in the art of dyeing, that logwood could be made to yield as good and durable colours as any other dyestuff.* This statement of course is incorrect, but it finds an echo in the statement of Mr. Jarman in the Cantor Lectures of 1876, when he says, "The use of proper mordants and a better knowledge of the properties of the colouring matters, have enabled dyers to obtain such fast and permanent colours with it (logwood), that the ban under which it formerly lay, arising from the fugitive nature of the colours obtained by the dyers who first used it, has long since passed away." The fact is that logwood colours are neither better nor worse now, than they were in the reign of Queen Elizabeth; the only new mordant for logwood colours discovered since her time is chromium, and that does not much improve the stability of the colour, although greatly preferable to the old copper mordant. The real change which has taken place is that light logwood blues, lavenders, and the like, which only admit of the use of a very small quantity of colouring matter,

* See Bancroft, ii., p. 340.

and which very quickly fade, on that account are not worked by respectable dyers, but all good logwood colours are dark colours and contain a comparatively enormous amount of colouring matter, so that it takes a longer time for the colour to fade and lose its primitive tone, for though logwood is of very great value as a dyeing material, its great weakness, even in deep blacks, is that it cannot long resist exposure to light and air.

As a blue colouring matter by itself logwood is therefore nearly useless on account of its instability; when condensed by increasing the strength of the mordants and the quantity of the colouring matter, it becomes a black possessing a fair amount of permanence, and is the principal ingredient in all common black colours; as a blue part in many compound shades both in calico printing and dyeing it is very useful, and as it only enters in small proportions in the composition of such colours its fugitive nature does not appear conspicuously.

For use in dyeing, logwood is rasped or ground. It is a very hard wood and not easily penetrated by water even when tolerably finely ground, so that the colouring matter is not readily dissolved from it unless it has been made to undergo a softening treatment previously. This is effected in practice by degging the ground wood with water and heaping it up in moderately warm places; fermentation accompanied by heating takes place, and the heating would proceed so far as to injure the wood if it were not

cooled down at proper intervals by turning it over and making fresh heaps of it. The large dyers who grind or rasp the logwood themselves consider that it should lay from three to six weeks in the degged state before being used; it is stated that by degging with a weak solution of glue instead of water, the logwood can be made ready for use in forty-eight hours.* It has been supposed that the long steeping and the heating which takes place produces some chemical change in the logwood, but if this be so the action will fall upon some of the non-colouring principles in the logwood and does not all affect or modify the amount or quality of the actual dyeing matters; the useful action is probably entirely of a physical nature and goes no further than softening the wood, rendering the colouring matter more easily accessible to the water. Logwood thus prepared is easily deprived of its colouring matter by a simple effusion of boiling water, and this is thought by large consumers to be the best way of extracting the colour, many do not even use boiling water, but instead, water at about 180° F. poured on the logwood in a tub or in a box with a sieve bottom, extracting it by simple percolation, and using the logwood liquor for dyeing. For common work no doubt the logwood would be more quickly exhausted by actually boiling it with water, but experience has shewn that for the finer blacks it is not advisable to use a prolonged

*Textile Colourist, iv., p. 50, from *Muster Zeitung*, No. 29, 1877.

boiling heat in extracting the logwood. In dyeing mourning blacks upon calicoes, the finely ground logwood is at once added to the dyebeck and heated up with the liquid and cloth together, no inconvenience resulting from the undissolved wood; but in woollens and velvets it would be nearly impossible to clear the particles of spent wood from the tissue, and it is necessary either to enclose the logwood in a bag or to use the clear decoction as above.

Besides its form of logs this colouring matter is also imported in the state of a syrupy extract, and also as a dry extract, and in these forms can be advantageously employed in many cases, although I believe the opinion to be well founded that these ready prepared extracts cannot be made to yield as fine colours as the freshly prepared weak extract which does not mark more than $\frac{1}{2}^{\circ}$ Tw. For printers' uses the logwood extract is prepared at various strengths, from 8° Tw. upwards. In all the concentrated extracts of logwood there is found upon dilution a quantity of tarry looking matter which does not readily re-dissolve even by boiling, and which should be separated from the liquid as it is likely to cause accidents both in printing and dyeing. Further, it may be observed that in old and strong logwood extracts it is frequently found that some of the colouring matter exists in the crystallized state. These crystals, which are very small, do not easily or quickly dissolve even in boiling water, and there is likely to be a great loss of colouring matter unless

the extract is boiled with water for a considerable time, so as to ensure the solution of these crystals.*

The chief use of logwood is in the black dye. Those blacks in which logwood is the only colouring matter used, upon whatever fabric dyed, are loose blacks, soon becoming brown or rusty upon exposure to the air. Upon cotton the mordant is usually a mixture of the acetates of iron and alumina. To avoid too much blue in the shade some yellow colouring matter may be added, as quercitron bark or fustic. Common black calico for linings is dyed upon an iron mordant alone, but generally a better colour is obtained by first sumaching the cotton according to the older method. Weaker iron mordants, dyed in logwood, yield shades of drab and grey. The common logwood black of the calico printer is a thickened decoction of logwood, with salt of iron for mordant, generally a mixture of nitrate of iron and acetate of iron. Nitrate of lime and acetate of iron is a good mordant. Of late years calico printers have made considerable use of a logwood black, with acetate and nitrate of chromium as the mordant, chlorate of potash being sometimes added as an oxidizing agent, and quercitron bark to counteract blueness and give depth. This black appears to be faster than an ordinary iron mordant black; it stands soaping and chloring very well, but as far as resisting ordinary

*This observation applies to other concentrated extracts, as those of quercitron bark, Persian berries, red woods, etc.; a neglect of the proper precautions may lead to great errors in testing the dyeing powers of these extracts.

wear and exposure to air and light, it is but little different from any other logwood black.

The use of bichromate of potash with logwood has been recommended as giving the black greater fixity in several cases. It is used as a mordant in woollen dyeing for blue-blacks, but there is reason to doubt that it does really improve the fastness of the colour. Logwood colours, in which bichromate has been used, sometimes shew a singular power of resisting the reddening action which strong acids have upon common logwood colours, but beyond that it is doubtful if any improvement is effected.

The quality of a sample of logwood is only to be ascertained by an actual dyeing test. The wood from different localities varies considerably in the quantity and quality of its colouring matter; the relative value of the regular commercial supplies being well understood in the trade.

Blue, from Aniline Salts.—A modification of aniline black, or rather a weak and incomplete aniline black, has been somewhat extensively worked as a substitute for indigo blue; it has not, however, had much success, it is unstable in its character, and not pleasing in its shade. It seems probable that with some more research it might be made into a permanent and useful colour.

YELLOW COLOURING MATTERS.

Nature is conspicuously richer in yellow colouring matters than in any other, and the dyer has, con-

sequently, a greater variety to choose from, but not a single one of them possesses the valuable properties of stability and permanency which characterise some one or other of the red and blue colouring matters. This is probably one of the chief reasons that yellow dyed goods have never been worn so generally as the other colours. It is difficult to conceive that there is any innate distaste in the human eye to yellow as a colour, but it is easy to understand that, as it is the colour nearest to white, that it soon becomes soiled in wear, and shews stains and discolourations more plainly than other colours, and as no yellow dye has yet been produced of sufficient permanence to withstand frequent cleansing operations in a satisfactory manner, it has been found practically unsuitable on these grounds for common use, and is consequently one of the colours very little worked by dyers or printers. The yellow colouring matters are, however, extensively used for mixed and compound shades, for greens, olives, browns, chocolates, &c. I shall give a short account of the chief yellow colouring matters, including some others which, though not strictly yielding yellow colours, seem naturally to belong to the same group, such as turmeric, annatto, etc.

Weld.—This dyestuff is of little practical importance at the present day, but it deserves mention as having been formerly the most commonly employed yellow colouring matter. It is a straw-like plant growing wild in many parts of Europe, but was cultivated for the dyer's use; it was grown in several

parts of England and sent for use in sheaves or trusses, being very bulky and unwieldy, the stalk only being useful. It gave a pure and tolerably fast lemon colour with alumina mordants, and was preferred by the dyers of the last century to Persian berries or fustic. To give a full yellow colour to wool or silk it required, according to Bancroft, double the weight of the fibre; upon the introduction of quercitron bark it gradually went out of use.

Quercitron Bark.—This is probably the most important and most largely used of the yellow colouring matters at present employed, although fustic occupies a very important position. Quercitron bark was first introduced from America by Dr. Bancroft about one hundred years ago, he devoted much attention to the investigation of its properties and its application to dyeing; government granted him a monopoly of its importation for a term of years, and it appears that he made a very liberal use of the powers granted, and supplied the material at a moderate price. At the expiration of the term, he applied for an extension on the ground of the small reward received for his labours, and offered to bind himself to supply the bark at a fixed price, his application was defeated in the Lords by the opposition of the dyers in the north of England after it had passed the Commons. The unfortunate discoverer derived no further benefit from his labours, but he may have had some satisfaction in finding that as soon as his right had lapsed, speculators got possession of all the

available bark and at once trebled its price to the dyers.*

According to Bancroft, quercitron bark is weight for weight eight or ten times as strong as weld, and about four times as strong as old fustic chips. It is delivered for consumption in a ground state, but rarely as a uniform powder, the stringy bark being difficult to completely grind up the commercial bark usually contains a large portion of the fine stringy bark along with powder; the powder contains the greatest amount of colouring matter; if the powder be separated by sieving, the remainder is perceptibly weaker in colour. Of late years a concentrated preparation of bark has been imported from America under the name of flavine. I do not know how it is prepared; it varies in quality, but some superior kinds which I have used were about fifteen times as strong as a good quality of bark, but for the purposes of garancine dyeing on calico to which I applied it, its price did not permit it to be used with economy. It is found useful in woollen dyeing, if for no other reason, because there are no woody particles to adhere to the wool as in the common bark. Dry and concentrated thick liquid extracts of bark are also imported to some extent, and may be profitably used for dyeing several shades of colour, but it is believed that they do not yield as good results as either bark or freshly prepared decoctions. For printers' uses an extract is made in this country which by concentration is brought to about 18° Tw.

* Bancroft, ii., p. 112, note.

Leeshing, on May 23rd, 1855, took out a patent for boiling quercitron bark with dilute sulphuric or hydrochloric acid, as he says, to improve it, the treatment being exactly analogous to that employed in making garancine from madder. I believe this product is manufactured to some extent, but my own experiments with a view to the use of the material in calico printing did not shew any advantage in the process; it is said that the product is better for some purposes because the tannin matters which would interfere in certain cases are removed.*

The chief consumption of quercitron bark is in garancine dyeing, where it serves as the yellow part in producing scarlets and chocolates. As yielding a yellow it is very seldom required in calico dyeing. It is employed as the best yellow for the neutral or lapis style, being dyed at the lowest possible temperature to preserve the purity of the colour. With tin salts a decoction of quercitron gives a yellow, or yellow-orange, which, when printed with garancine mordants, supports, to some extent, the fixing and dyeing operations, and the tin, taking up some red from the garancine, forms what is known as the garancine orange, at one time largely worked. In steam colours for calico, delaine, and wool, extract of quercitron is used for the yellow part of browns, chocolates, tans, and other compound colours. As before stated

*Schaeffer states that the dyeing power of quercitron is more than doubled by treatment with acid, a result quite at variance with my experience. See *Bull. de Mulh.*, xxvii., p. 411; in *Schützenberger*, ii., p. 440.

flavene is the preferable form in which quercitron bark is used in woollen dyeing, its use, however, is nearly confined to scarlet dyeing, fustic being more generally used in the yellow part in compound shades; flavine, however, is used for pure yellows.

Fustic.—Some confusion has arisen from the use of this word for two different substances called “old fustic” and “young fustic.” What is properly called fustic is a dense, solid, and large sized yellow wood, from a tree which grows to considerable size and solidity in Central America and the West Indies. The young fustic (Fr. *fustet*) was probably so called because it was small, never growing large, being actually a shrub of the sumach kind; it is not nearly so much used in England as the real fustic.

Fustic is rasped or ground like logwood, and prepared for use in the same way; it is largely employed in piece-dyeing, both in cotton and woollen goods, but hardly at all used by printers. It is the favourite yellow part for most compound shades which require it, and is a good deal used along with logwood and sumac in the black dye, but its chief consumption is in shades of brown upon wool, the mordant for it being the bichromate of potash, sometimes with alum, and if required, followed by a “saddening” or browning with a salt of iron. It is preferred to quercitron bark as giving a fuller bodied, denser, or less transparent colour.*

* For many illustrations of the use of fustic in woollen dyeing, see Jarman's Cantor Lectures. Journ. Soc. of Arts, 1876; abstracted in Textile Colourist, ii., p. 323.

Persian Berries.—This is the common name in England for a berry about the size of a pea, which is also known under the name of French berries and Turkey berries, and sometimes as yellow berries. Varieties of the berry are prescribed in the oldest dyeing receipts that we possess, and it is still employed to some extent in fancy woollen dyeing. Its chief consumption, however, is for printing purposes, being the liveliest and brightest yellow colouring matter available, and free from a certain amount of red which is present in most other yellow colouring matters. It yields an orange yellow with tin salts alone, but is seldom employed as a yellow; it enters as the yellow part in most of the bright colours used in the steam styles, especially green. It possesses but little permanence, resisting exposure to air and light better than it does washing with soap. It is very soluble in water, and the decoction is usually made by the printer as required, by simply boiling the berries in water. Good qualities are very rich in colouring matter, and a solution marking 5° or 6° Tw., can be readily obtained without concentrating.

Annatto.—This is a manufactured preparation as imported; it gives rich and pleasant shades, especially upon silk; it fixes upon all fibres without mordant, but the colour which it yields is so fugitive that its employment is restricted to fancy styles, or as a bottom or top, to modify and enrich other dyed colours. It is prepared for use by dissolving in an alkaline solution, as it is nearly insoluble in water,—caustic or

carbonated alkaline may be used. In many receipts, especially for printing, soft soap is prescribed in mixture with caustic alkali. Acids change the dyed colour, but do not discharge it, it resists, in fact, tolerably well detergent agents, but soon fades when exposed to light and air. The colour which it gives to cotton resembles a medium buff, upon silk it gives flesh and salmon colours. Its pure colouring matter is called bixine, and under that name an improved preparation of annatto is sold as a dry cake, which is much more powerful than the best pasty annatto as usually imported.

Turmeric.—This colouring matter is, like the last, one of the few which fix upon vegetable fibre without the aid of mordants; it is rich in colouring matter and gives good shades of yellow, but is so exceedingly fugitive that its use is confined to very few styles. Its principal use perhaps being in silk dyeing, where it frequently serves as the yellow part in greens, olives, and some other colours.

Besides the above vegetable yellow colouring matters there are a great number of others known, but none of them, as far as I am aware, have received practical application, and do not call for notice in this place.

Chrome Yellow.—Though this colour is one produced by chemical action upon the cloth and differs greatly from any of the other colouring matters in its chemical characters and method of fixing, it is

most properly considered in this place. The chrome yellow is a chromate of lead, and to bring it into analogy with other dyed colours, the lead may be looked upon as the mordant, and the chromic acid as the colouring matter.

The chrome yellow upon silk was first discovered or applied in 1817, by Lassaigne, who thought it could not be applied upon cotton.* Bichromate of potash at that date was a costly drug, but the colour was soon recognized as one of capital importance, and the proper means of applying it diligently worked out. It was first used on cotton prints by Koechlin Brothers, of Mulhouse, in 1820, who also discovered how to use the discharge chrome yellow upon such colours as could withstand for a time the action of bleaching powder solution, which was in fact only a development of known methods.† Numerous ingenious applications of this colour soon followed, and it became of extraordinary utility for varying the colourings of many styles of prints, especially the indigo styles. It is valuable not only for the fulness and richness of its tone, but also for its solidity and permanency, in these latter characteristics being

* Thomson's Annals, xvii., p. 73, Vol. i.; New Series, January, 1821, from Ann. de Ch., Vol. xv.

† See formal claim Bull. de Mulh., 1871, p. 227. In this document it is also claimed for MM. Koechlin that they were the discoverers of the acid and bleaching powder discharge upon Turkey red, and the date of 1811 is given. Thomson's patent for this style is dated March 3rd, 1813; in his patent dated February 4th, 1815, he points out how various oxides may by this method be deposited where the white is discharged, and afterwards dyed with various dyewoods.

greatly superior upon cotton to any other yellow colour known. It is, however, of little or no value upon either silk or wool, and is scarcely ever applied to them.

The processes of fixing chrome yellow are well understood, and need only be briefly mentioned. They consist in first fixing the lead basis, and then dyeing it in the bichromate. In calico printing the usual practice is to print on a mixture of acetate and nitrate of lead, and to fix in cold dilute sulphuric acid, if there is no other colour in combination with the orange; but if there are other colours which will not support an acid treatment in the design, the fixing may take place in sulphate of soda tolerably hot and concentrated, or in some alkaline liquid as dilute ammonia or carbonate of soda, but in general sulphate of soda is preferred. For heavy and dark oranges the fixing of the lead requires care, for the lead salts being very soluble in water, and not being at all fixed by ageing, require to be immediately made insoluble; therefore, in the case of single oranges, it is recommended to use the sulphuric acid as strong as possible, say as high as 10° or 12° Tw., the only difficulty attending the use of acid at such a strength being in the washing of it completely out. For the same reason in the case of fixing with sulphate of soda, it should be used strong, and nearly boiling. In either of these two cases the lead is of course fixed as insoluble sulphate of lead. In piece dyeing or in yarn dyeing, it is perhaps most common to fix the

lead by means of lime. There are many variations in the mode of procedure, but usually the cotton to be dyed is first steeped in clear lime water, then in solution of acetate of lead, and then again in clear lime water, and the alternate steepings repeated until it is thought that sufficient of the lead basis has been fixed upon the fibre. In this case the lead is mainly deposited as oxide of lead. The common brown acetate of lead is usually employed, but there are many receipts in which the acetate is previously boiled with a certain quantity of litharge (oxide of lead), which it dissolves, forming a sub-acetate of lead, in which the proportion of lead to acetic acid may be twice or thrice as great as that existing in the common acetate, and perhaps some economy in time and material is effected.

The lead being well fixed, the dyeing in the bichromate is simple, the cloth or yarn being worked in a warm solution of it until the colour is well developed. For plain dyeing a richer effect can be obtained by repeating the dyeing, by passing in lead solution, and then without washing passing again in the bichromate.

The colour thus obtained is a lemon yellow, and if that shade is required the operation of dyeing is completed, but the chrome yellow is in nearly all cases only a step to the production of chrome orange.

Chrome Orange.—This colour can be obtained directly by passing the lead mordanted cloth through a boiling alkaline solution of chromate of potash, but this is rarely done on account of difficulties in getting

a uniform and regular colour; the production of the yellow is nearly always the first step in dyeing the orange. The yellow is converted into orange by simply passing it through a boiling caustic alkaline solution; usually this is a separate and distinct process from the dyeing, and carried on in different vessels, but it is quite practicable to obtain the orange in the same vessels in which the yellow is dyed by adding caustic soda or milk of lime to the liquor and continuing the heating; safety, however, is best secured by washing out the yellow dyed goods and then passing them through boiling lime water or weak milk of lime. The action of soda or lime is to decompose the neutral chromate of lead by removing one-half of its chromic acid and producing the so-called di-chromate or basic chromate of lead. Considering that the chromic acid is the colouring matter in this case, and that the chrome orange is a much deeper and richer colour than the chrome yellow from which it is derived, it appears a paradoxical effect; but the colours of chemical compounds, even of the same elements, frequently have no resemblance when the proportions are changed, as witness the colours of the various compounds of lead with oxygen, which are for one oxide white, another red, and another chocolate. The neutral chromate of lead is distinctly a different chemical compound from the basic chromate, it has a different colour, and we shall perhaps never know the reason why. The action of the alkalies upon chrome yellow, unless carefully

regulated as to strength, time, and temperature, may pass the point required to fully develop the orange, and, taking away more chromic acid than necessary, impoverish the colour, and eventually quite destroy it. This is a matter entirely for the practical dyer to control and requires careful attention and continual inspection of the colour as it is passing through. To prevent "stripping" of the colour at the commencement of the raising it is advisable to add a small quantity of bichromate to the lime water or milk of lime.

Combination of Chrome Orange with other Colours.—I will only briefly refer to three principal cases. The combination with dipped indigo styles has been mentioned p. 227; the discharge yellow or orange upon Turkey red or ordinary madder red or pink is obtained by printing a mixture of nitrate of lead with tartaric acid, the lead being fixed and the madder colour discharged by passing the printed cloth through solution of bleaching powder mixed with a sufficient amount of free lime; the yellow is obtained as usual by chroming. The combination of chrome orange with dyed madder work, which made its first appearance about 1864, constituted an important style for several years, but since the extended use of alizarine and madder extract with pigments created a similar and cheaper style it has nearly disappeared. A brief account of this style, which was somewhat difficult to produce at its best, will suffice. For the orange a colour composed of mixed nitrate

and acetate of lead was printed along with the usual madder mordants; to give greater certainty in fixing the lead many houses prepared the cloth with solution of sulphate of soda perfectly neutral and free from iron. After the usual ageing the pieces were passed in hot sulphate of soda with chalk, and sometimes with dunging salt, or first through sulphate of soda and then through some dunging salt or cow dung and cleansed. The next step varied, the goods might be chromed at a comparatively low temperature to bring up the yellow, which I think the preferable manner, or they might go straight on to the usual madder dyeing. The only real difficulty in the style consisted in the lead basis taking up a portion of the colouring matter in the dyeing, which had to be cleared off in order to get the orange of a pure shade, and in some cases this clearing was attended with much trouble, this doubtless being frequently traceable to want of sufficient cleansing before dyeing, and the presence of mordanting oxides in the dyebeck. When all was in right condition a couple of soapings would clean the lead mordant, shewing it a more or less pure yellow if previously chromed, or a pale pinky shade if not chromed. The orange was developed by passing through boiling lime with chromate of potash, and the white and the orange afterwards brightened by as strong a chloring as the other colours would stand. This orange was also worked as a resist orange under purple covers, in this case the colour might be either all nitrate of lead and no acetate,

which sufficiently well resisted light shades, or tartaric or citric acid might be added in small quantity, care being taken that the cloth was not too highly heated in the drying to avoid risk of tendering it from this somewhat corrosive mixture.

Pigment Orange.—Ready prepared chromate of lead is used as a pigment colour, and fixed by albumen. Red lead or minium is also largely used for the same purpose, and gives good results when properly prepared. The weakness of this latter pigment is that it is destroyed by acids even when very diluted, it loses its orange colour and becomes pale chocolate or brown coloured, and can be thus easily distinguished from the real chromate of lead. In the course of steaming it is liable to be completely spoiled if the steam becomes acid from the disengagement of acetic acid from other colours, and this is simply owing to the splitting up more or less completely of the red lead into a salt of the protoxide and the puce coloured peroxide.

Iron Buff.—This colour may be briefly considered in this place as having a close resemblance to some of the yellow colours. It is produced in printing from a mixture of acetate and sulphate of iron, which is decomposed upon the cloth by means of alkali, the protoxide being then made insoluble fixes on the fibre where it is speedily changed into the state of peroxide with its characteristic buff or chamois colour. The depth of the buff colour and its character, as obtained

from a given strength of mordant, depends in a great measure upon the activity of the fixing liquor used. If a yellowish shade is required, soft in appearance and without harshness to the feel, chalk and water may be used to fix the colour, this is suitable to padded buffs of light shade; if a stronger and bolder colour is required, carbonate of soda varying in strength from 2° to 8° Tw. may be used, and for the darkest and reddest shade of buff caustic soda at 2° or 3° Tw. may be used.

The iron buff in piece dyeing is obtained by working alternately in iron solution (generally nitrate of iron) and alkaline liquids, as lime water or dilute ammonia. The buff colour from iron is only applicable to cotton goods; it is very stable to the action of air, light, and alkalis, but it gradually loses tone by washing, probably from mechanical causes detaching the pigment; by soaping iron buffs they are improved in appearance, the harshness is palliated, and I believe the colour is faster.

COLOURING MATTERS YIELDING COMPOUND SHADES.

For the purposes of this work it is assumed that red, blue, and yellow are simple colours, and that all the remaining colours are compounded of these elements.

Purple Colours.—Red and blue together give the class of colours which may be called purple when somewhat concentrated and when less dense lilac, violet, etc.* Except the madder purple, which has

*The nomenclature of colours is very defective and Chevreul's systematic

been treated of, and to a small extent archil, alkanet, and logwood, there is no single natural colouring matter which yields purple dyes, and these colours are consequently produced by the mixture of red and blue colouring matters, as for example, cudbear and extract of indigo, cudbear and logwood, logwood and peachwood, fast indigo blue and cochineal, etc. The artificial colouring matters are at the present time the source of the richest and finest shades of purple.

Green Colours.—The only vegetable green colouring matter applicable to dyeing is the Chinese green. How long the Chinese may have had possession of this colour is not known; it was only in 1848 that it was known in Europe, attention having been drawn to it by M. D. Koechlin, who having examined a specimen of dyed Chinese calico, found that the colour was not compounded of blue and yellow as all the greens we knew up to that time were, and declared with his usual sagacity, that it was some dyestuff quite unknown in Europe. The material was enquired for and obtained, or at least a certain manufactured article was imported called Chinese green, which was a concentrated preparation derived by circuitous processes which included dyeing calico with the native product and taking off the colour again. It was sold at a high

nomenclature is too little understood in England to be used. With regard to the real colour of Tyrian purple, Gibbon, in the 48th chap. of the *Decline and Fall of the Roman Empire*, has "In the Greek language purple and porphyry are the same word; and as the colours of nature are invariable, we may learn that a dark, deep red was the Tyrian dye which stained the purple of the ancients;" but unfortunately for this definition porphyry is of all colours, and even the red sort has a variety of shades.

price, and to some extent used by the highest class of silk dyers. Experience in its use did not shew any special advantage and it was never largely employed. Upon cotton it was an extremely loose colour and of no value, it has only at this time a scientific and historical interest.

After the introduction of the above green colour, attention was turned to vegetable greens, and it was found possible to fix the green colouring matter of grass and other herbs upon tissues, but up to the present time there is not the least prospect of the abundance of green in nature being utilized for the purpose of dyeing.*

Mineral greens, which can be applied by the methods of dyeing and printing, are comparatively numerous; some of them have been employed in the earliest processes of which we have any exact record. These older ones are all derived from copper, and would appear to have been essentially some insoluble salt as a basic acetate; afterwards the arsenite of copper green came into use and was pretty largely employed, as fixed upon the tissue by dyeing process, not to speak of its use as a pigment; at a still later date fatty soaps of copper were used as green colours in calico printing. All the copper greens have been long since given up. The chromium greens next followed. I believe they were first introduced into

* The literature upon Chinese green is very extensive. Verdeil's incomplete patent for extracting green from artichokes and thistles is dated June 3rd, 1856; Hartmann's and Cordillot's experiments upon grass, etc., Bull. de la Soc. Ind. de Mulh., xxvi. p. 283.

this country, from Bohemia, about 1840,* and were known in England under the name of Victoria green. At first the solution of chromium was prepared by reducing bichromate of potash with tartaric acid, afterwards the bichromate was reduced by arsenious acid, and still more lately organic reducing agents have been used, such as sugar, starch, and glycerine. The cloth being printed or padded with the solution of chromium, the oxide was fixed by a passage in alkali, such as lime, or preferably, in a strong solution of carbonate of soda. The chromium green thus fixed is an opaque colour of low intensity, and without brightness, but pleasant to the eye, the reduced shades being more properly a greenish grey than green proper; when suitably thickened and fixed it is one of the most stable colours. None of the attempts which have been made to obtain a bright green from oxide of chromium precipitated from its salts in the moist way have been successful. Francillon patented, May 28th, 1853, the printing of bichromate upon calico, and exposing it in a damp state to the action of sulphurous acid gas or other deoxidizing agents. A process for a steam chromium green was patented by Clark (from Dehaut), October 19th, 1865. Bichromate of potash and ammonia, with phosphate of ammonia, mixed with glucose or other similar deoxidizing body, was to be printed, by steaming the chromic acid was said to be

*See Kurrer in Chem. Gaz., viii., p. 461; Newton's Journal, 1850. C. Koechlin states that they were employed in Mulhouse as early as 1832; Bull. de Mulh., xxv., p. 399.

reduced and oxide of chromium fixed. By passing the already fixed chromium oxide in salts of copper some increased intensity of colour could be obtained, but it has not proved of any advantage.

Pigment Green.—This is essentially the same oxide of chromium chemically viewed as the above, but prepared in the dry way at a high temperature instead of by the wet way at a low temperature, and is surprisingly different to it in depth and brightness of colour; it is a bright and vivid green, and has proved a most valuable pigment for the printer, for being insoluble it can only be used as a pigment and not as a dye. A bright chromium green was manufactured in France on a small scale and by a secret process some years before it was independently and nearly simultaneously discovered by Guignet and Salvétat. The former of these chemists had the priority and secured a patent for the process, which consisted in fusing bichromate of potash with boracic acid. The English patent communicated to Gilbee is dated July 28th, 1858. Another process, communicated by Kestner, who had the manufacture of this pigment from the commencement, was patented March 21st, 1868. In the newer process, instead of bichromate of potash, one part of the green hydrated oxide of chromium is heated with six parts of boric or boracic acid, the mixture fuses forming chromic borate, which is decomposed when heated with water, producing the so-called emerald green or Guignet's green. Although the commercial pigment nearly always

contains some boric acid, that acid is not essential to its constitution, it being actually a hydrated oxide of chromium when carefully purified.

This green is sold and delivered for consumption as a stiff paste, which only requires mixing with albumen water to be ready for printing. Some continental makes of this pigment work badly in the printing machine, "sticking" in the engraving and giving bad impressions; whether this be caused by adulteration, which it is known is practised, or whether it may arise from an imperfect system of manufacture, I do not know. Reference has been made to this fault of colours when treating of colour mixing, but here I may refer to an instance which occurred in my experience. On commencing with a fresh cask of the green, which was of German make, thickening with an albumen solution of known goodness, it was found in printing a rather fine cover that the colour would not work; before half a dozen yards of cloth had gone through the machine the engraving was filled and only the barest impression obtained, all the usual plans were tried to improve the colour but with no good result, and the machine was stopped. I examined the paste with several reagents and found that it effervesced rather strongly with acids, containing an earthy carbonate; upon carefully adding nitric acid to the paste warmed up, until it had a faintly acid reaction and ceased to effervesce, and then mixing it with albumen, I was pleased to find that it worked perfectly well and printed more than 1,000

yards without the least trouble. The already thickened colour was treated with acetic acid and worked well.

This green pigment is of an extremely stable character in itself, and capable of resisting air, light, acids, alkalies, etc., better than any other pigment used in printing; it was generally considered unattackable by reagents, and some surprise was created a few months ago when M. Balanche shewed that the green was acted upon by solution of bleaching powder and dissolved, being oxidized into chromic acid. This interesting discovery does not however affect in the least the reputation of the green for fastness for all practical purposes, since the bleaching powder solution must be very strong to act upon it, so strong in fact that the cloth is injured, and the fact cannot be even utilized for bleaching out the green if it was desired.*

This is the only simple green at present in use (the artificial colours excepted), all other green colours are produced by a mixture of blue and yellow, employing some one or other of the colouring matters already mentioned.

Orange Colours.—There are no orange colouring matters in use beyond those which have been already mentioned as belonging to yellow. In practice these colours not included amongst the yellow ones are obtained from a mixture of red with yellow colouring matters applied together or separately.

*See *Textile Colourist*, iii., p. 117, from *Bull. de Rouen*, iv., p. 421.

The foregoing compound colours result from pairs of the elementary colours ; when the whole three are mixed together we have brown in all its shades, grey, and black. Though actually the very extensive range of colours which may be said to belong to the class of browns, as well as greys and black, are for the most part dyed from a mixture of different dyestuffs whose colouring matters together form the compound shades, there are some single dyestuffs which themselves yield some of the shades, and are properly considered in in this place.

Catechu.—This may be looked upon as the source of an extensive class of browns, fawns, drabs, greys, etc. It is an important colouring matter for the cotton dyer, not only for the number of shades which it yields, but also for their generally good character for stability ; for woollen it is very little used, and for silk almost only in the black dye. In calico printing it has been of essential service as the source of numerous shades of brown, grey, and drab, whose method of fixation and fastness enabled them to be combined and worked with other fast colours as madder and garancine.

Catechu is only of modern introduction as a dyeing material into Europe ; it had been long known in the *materia medica*, and in the East had received practical applications in dyeing and tanning. The earliest date named for its use as a colouring material in Europe is 1801, when it is mentioned as a tannin matter *sui generis*, by Proust, and also as a dye for silk. It was also known to Davy as a tannin matter

at about the same date; he says also that it would dye linen, but he did not pursue the question of dyeing. In 1806 it was employed by Schaeppler and Hartmann in calico printing, the process being described in Dingler's Polytechnic Journal for 1815, but it did not come into regular use until about 1830, and even then but few houses understood how to apply it properly, and it was a kind of secret. In the Peel Park collection of print styles current in England, I did not observe any catechu colours previous to the year 1847.*

Catechu fixes with great facility upon fibre, and in a manner different from any of the other colouring matters heretofore considered. It is soluble in water, and if cotton be impregnated with the solution all that appears necessary to cause an intimate union of the colouring matter and fibre is to oxidize in one way or other the colouring principle; thus light shades can be dyed by simply working cotton in a solution. For darker colours a more active oxidation is required, and this can be accomplished in several ways; passing in alkalies, as in lime water or caustic soda, and exposure to air fixes the colour to a considerable extent, and no doubt this is a case of oxidation, but generally more direct oxidizing agents are employed, the chief being bichromate of potash for application subsequent to the catechu, and salts of

* See Nicholson's Jour., ii., p. 198, for 1802, from Ann. de Ch., xlii., p. 89. Davy in Philos. Transac. for 1803; in Nicholson's Jour., v., p. 271; also Bull. de Mulh., xii., 351; xxii., p. 311, etc. Leuchs, in 1829, refers to its use in printing with verdigris and salammoniac.

copper for application with the catechu upon the fibre. In many cases of dyeing a mixture of copper salts and bichromate is used.

The shades of colour obtained from catechu have a very wide range both in quality and intensity, depending partly upon the amount of catechu present, partly upon the nature of the oxidizing agent employed, and partly upon the use or not of mordants of alumina and iron in conjunction with the catechu, and partly also upon the quality of the catechu itself. It is not possible in this book to go into all the details of the different methods of applying catechu; only some illustrations of the principal cases can be given.

In calico printing catechu has been largely used in combination with madder and garancine colours. The fixing agent in this case is usually nitrate of copper or acetate of copper, the regular action of which is remarkably assisted by the presence of a considerable quantity of salammoniac. The most suitable thickening for medium shades is gum Senegal; with paste thickenings darker colours can be obtained, but they have a comparatively coarse and rough appearance, and are not easy to print. The printed colour which is pale at first becomes darker by ageing; the time of ageing varies according to the depth of colour; for the usual shades twenty-four hours' moderately warm ageing is sufficient, for very dark colours and massive designs a much longer ageing may be required. The colour thus printed

will resist the usual dunging, washing, dyeing, and clearing process required for the production of garancine and madder colours. An additional oxidation may be effected, if desired, by dissolving a small portion of bichromate of potash in the dunging liquor, or the goods may be passed in cold bichromate solution after dunging. By this treatment the catechu is no doubt more effectively fixed; the dangers are that some injury may be done to the mordants combined with the catechu colours, and the shade of the catechu itself somewhat dulled; if a lively yellow shade of catechu brown is required, there should be no bichromate used. The so-called catechu drab colours used in calico printing in combination with madder and garancine are obtained by adding a salt of iron to the ordinary brown colour, and diluting with gum water, according to the shade required.*

The only difficulties presented by catechu colours in printing are, firstly, those arising from a tendency they have to "stick" in the engraving, and give a bare impression; and, secondly, defects in ageing, when the colour not being well fixed, a great portion is lost in the dunging and dyeing, giving only light shades when finished. When the colour mixer is troubled with catechu brown sticking in the engraving, he may suspect the gum in the first place, and if the fault cannot be fixed there it will probably be traceable to an inferior quality of catechu. In receipts

* A collection of receipts for catechu colours may be found in the *Textile Colourist*, ii., p. 34.

dating twenty or thirty years ago it is frequently prescribed to boil the catechu and water together for several hours, with or without the addition of acetic acid, so as to obtain a good solution. This was with a view to avoid sticking it; but catechu is easily soluble in water, and average qualities should not require more than a short boiling of say half an hour to produce a perfect solution, which, when thickened, should work well in the machine. The common method of preparing catechu colours amongst English colour mixers is to prepare a strong standard solution of catechu containing 6 lb. or 8 lb. of catechu per gallon, and mix this with gum water; but this method is not suitable for all kinds of catechu, and likely with some qualities to give colours which work badly. If colours so prepared do not work well a modification of the process of making the colour will generally be found to be a perfect remedy for sticking in. Let a solution of the catechu be made at the lowest strength required for the ordinary run of the colour, say at $2\frac{1}{2}$ lb. to 3 lb. per gallon of water; after boiling for a short time the solution should be allowed to settle for three or four hours, or as long as it keeps hot, and then decanted from the bottoms and thickened with dry gum at a boiling heat; the salammoniac may be dissolved along with the gum, and the thickened liquid strained while hot. A strong solution of catechu in water separates upon cooling into a transparent liquid and a bulky deposit; in allowing a hot solution to stand for the purpose of

settling it must be decanted before this deposit commences to form, for it is an essential part of the colouring matter.

Defects in ageing catechu colours may be mostly traced to want of moisture in the ageing rooms or want of warmth. They are not colours which lose anything in ageing, like the ordinary mordants, but, on the contrary, become fixed by the addition of oxygen, which is commenced by the action of the copper salts in the colour, but can only be completed by the free access of air. In many instances it is found useful to add a deliquescent or hygroscopic salt to the colour, as nitrate of lime, muriate of lime, or acetate of lime, the latter salt not in itself hygroscopic, becomes so in contact with the nitrates and chlorides in the colour.*

The action of copper salts and salammoniac in fixing the colour of catechu, as well as other colours, was investigated many years ago by MM. Camille Koechlin and Plessy.† They proved that salammoniac was useful in increasing the oxidizing powers of the copper salts, but in what way could not be shown. The copper acts directly as an oxidizer to a small extent, and also conveys oxygen from the air, which it continues to do until the organic substance in contact has reached a certain definite state of

* Penney, January 22nd, 1863, patented the use of a mixture of chloride of calcium (muriate of lime) and nitrate of copper as an improved fixing agent for catechu colours.

† Bull. de Mulh., xxii., p. 311. Journ. de Pharm., December, 1850. Chem. Gaz., ix., p. 177.

oxidation. Other chlorides, such as common salt, possess the same properties, but in a less degree.

In piece dyeing catechu is fixed mainly by means of bichromate of potash, and the same oxidizing salt serves as the fixing agent in nearly all cases of printed colours where catechu shades, not to be dyed, have been employed. Soda and lime are also used as fixing materials. Haigh and Heaton patented, September 29th, 1863, the process of using lime as a fixing agent for catechu colours, and dispensing with bichromate of potash.

From a chemical point of view catechu may be looked upon as holding a position between colouring matters and astringent or tannin matters, and possessing some of the properties of both; as a tannin matter it can receive few applications in dyeing on account of its colour, but it is profitably used in that capacity for dyeing black and dark colours upon silk. In common with the real tannin matters it has the property of fixing some of the artificial aniline colours upon cotton, and has been used in conjunction with purple to obtain an imitation of madder lilac, and with fuchsine or magenta to produce a chocolate similar in appearance to that dyed with garancine. These colours were fixed by steaming and chroming, but were of a low class, soon fading in wear.

There are some other colouring matters which might be mentioned as belonging to the same class as catechu, but they are of little or no practical impor-

tance, an enumeration of them and references to sources of information will be found in another place. Mention may here be made of extract of chestnut, which though little known in England, is largely employed on the Continent for the black dye. Mahogany wood and bark has been proposed for dyeing brown colours in Dreyfus' patent of July 30th, 1872, and Raves' of November 4th, 1872, but never largely employed.

Astringent or Tannin Matters.—The essential principle of the various tannin matters used in dyeing is tannic acid, which is itself devoid of colour, but with salts of iron gives a bluish-black colour when the solutions are somewhat concentrated, and a bluish-grey when diluted. The purest and strongest source of tannic acid is the common gall-nut, which may contain more than half its weight of the real tannin principle nearly free from colour. There are a variety of galls from different regions, as well as other excrescences from trees, differing in shape but possessing the same characters in a less marked degree, generally however distinguished by absence of colour. The natural fruits as well as the leaves and shrubs which contain a sufficient amount of tannin principle to be useful in dyeing contain generally some other colouring principle, as for example, sumach and myrobalams, which give a yellow colour; valonia and divi-divi also give coloured solutions. The only colours which the proper tannin matters give in dyeing are black and

grey; the impure tannin substances may yield various colours depending upon the peculiar matters which accompany the pure tannin, but with an iron mordant the grey or black so far dominates the other shades that they always produce dark colours.

Sumach is probably the most important of the tannin matters used in dyeing, since the demand for gall-nuts in other trades has made them too costly to be commonly used. It contains the tannic acid in a tolerably pure state, and in good qualities there may be as much as 20 per cent. of it present. There is also a notable quantity of a yellow colouring matter in sumach which easily fixes upon alumina mordants, and so far affects iron mordants that they yield only an impure shade of grey or black when dyed with this substance.

Myrobalams contain tannic acid in a tolerably pure state, and this astringent nut or fruit when reduced to a fine powder (which requires special methods of grinding on account of its great hardness) can be used as well as sumach for fine colours in piece dyeing. These and other kinds of tannin substances are seldom used except in conjunction with other colouring matters, and generally as the grey or darkening part in compound shades.

Sumach in weak solutions made by "scalding," or treating the herb with hot or boiling water, as is usual with dyers, is particularly liable to injury from a species of fermentation which takes place after a few hours' standing; it is supposed that the tannic

acid changes into gallic acid, which is nearly useless if it is not positively injurious to the dyer. Hence dilute decoctions cannot be kept beyond one or two days in a good condition, and sometimes a few hours suffices to make them unfit for use. Concentrated extracts are not subject to the same inconvenience, nor do weak solutions of them appear to be so easily injured as those made direct from the leaf, probably the fermenting principle may have been destroyed by the heat used in concentrating them. Practical dyers prefer to make their own decoctions from day to day as they require them.*

COLOURS FROM ANILINE.

The first record of the practical production of a colour from aniline is in a patent to Perkins, dated August 26th, 1856, which was for treating sulphate of aniline with bichromate of potash to produce the substance afterwards called aniline mauve. In the same year, Mr. Perkin says "the first experiments upon the application of this dye to the arts of dyeing and calico printing were made at Perth and Maryhill."† So much that is easily accessible has been written upon the aniline colours of late years that I deem it superfluous to go over the ground in the tracks so well trodden by numerous writers, and shall therefore only select a few points which seem of the greatest practical

* Tannin as a mordant and as a fixing agent for some colours has been previously treated upon, vol. i., pp. 284, 290.

† British Assoc., Glasgow, Sept., 1876.

interest. For purposes of reference I give a list of the numerous patents in the order of their date as I find them in my note book, dividing them into two lists, those which concern the *making* of the aniline colours, and those which refer to the *application* of them. Aniline black being considered radically different from all other aniline colours is not included in these patents, and forms a separate article. Artificial colouring matters made from naphthaline and other substances are included in a separate list of patents.

- 1856, August 26th.—Perkin: Manufacture of colour from sulphate of aniline by means of bichromate of potash. No. 1,984.
- 1859, April 12th.—Brooman: A communication from Renard Frères for making a red colouring matter (fuchsine) by boiling a mixture of aniline and anhydrous bichloride of tin. The use of bichloride of mercury, perchloride of iron, and protochloride of copper is also claimed. No. 921.
- 1859, April 30th.—Williams: Besides quinine, cinchonine, strychnine, brucine, etc., as sources of colouring matter, patents the treating of aniline and analogous bodies with permanganate of potash, so as to obtain a purer colouring matter than is yielded by bichromates of potash. No. 1,090.
- 1859, May 7th.—Kay: Preparation of a colouring matter called harmaline, made from sulphate of aniline by treating it with peroxide of manganese, precipitating by ammonia, and dissolving out by alcohol. No. 1,155.
- 1859, May 13th.—Beale and Kirkham: Production of colouring matter by treating aniline and its salts with chlorine and hypochlorites. It is stated that not only purple or violet colours, but also drabs, greens, blues, and reds may be obtained. No. 1,205.
- 1859, May 25th.—Price: Production of violet, purple, and rose colours from aniline, by the use of sulphuric acid, and the peroxide of lead, peroxide of manganese, etc., with subsequent purifying processes. No. 1,288.

- 1859, July 2nd.—Williams: For modifications in the methods of purifying the crude colouring matter obtained by the action of bichromate of potash upon aniline, and the use of turpentine and caoutchene in the process. No. 1,583.
- 1859, October 27th.—Brooman, from Renard Frères: For making fuchsine by means of bichloride of titanium and several other metallic salts. No. 2,471.
- 1859, November 1st.—Perkin: Production of a red colouring matter from aniline by boiling it with bichloride of mercury. No. 2,492.
- 1859, November 15th.—Perkin, from Knosp: Production of a crystalline red colouring matter by boiling aniline with anhydrous sub-nitrate of mercury or other salts of mercury mentioned. No. 2,594.
- 1859, November 28th.—Brooman, from Renard Frères: Production of a red colouring matter by boiling aniline and its homologues with sulphate of tin and a number of other metallic salts. No. 2,694.
- 1859, December 3rd.—Smith, from Schlumberger: Production of fuchsine by boiling aniline with metallic nitrates, preferably nitrate of mercury, or with iodine and iodides. No. 2,746.
- 1859, December 10th.—Heilmann, from Gerber: Production of a colouring matter called azaeline by boiling aniline with various salts and oxides, of which a great number are mentioned. No. 2,800.
- 1860, January 18th.—Medlock: The use of dry arsenic acid with aniline for the production of colouring matters. No. 126.
- 1860, January 24th.—Hughes, from Depouilly and Lauth: Production of colours from aniline by decomposition of the nitrate of aniline by distillation. No. 176.
- 1860, January 25th.—Nicholson: Production of colours from aniline by means of a strong solution of arsenic acid. No. 184.
- 1860, January 28th.—Nicholson: Production of colours from aniline by means of nitric acid, similar to No. 176 above. No. 224.
- 1860, May 26th.—Laire and Girard: Acting upon aniline with arsenic acid and water to make red and violet colours. No. 1,300.

- 1860, May 26th.—Dale and Caro: Production of aniline purples by means of chloride of copper, and aniline reds by means of anhydrous nitrates and phosphoric acid. No. 1,307.
- 1860, July 5th.—Squire: For treating aniline salts with finely divided peroxide of mercury. No. 1,625.
- 1860, August 11th.—Smith: Use of red prussiate for making a purple colour; use of the oxides of tin, iron, and mercury for red colours; also, chloride of antimony, and replacing antimonous acid by teroxide of bismuth. No. 1,945.
- 1860, August 17th.—Smith: Production of purple colours from aniline by acting upon it with a solution of chlorine in a two per cent. solution of sulphate of soda, or by simple chlorine water. No. 1,990.
- 1860, November 14th.—Gratrix from Paraf: Production of purple colours by acting upon aniline with nitrate of copper, and red colours by means of nitrate of antimony. No. 2,794.
- 1861, January 10th.—Williams: Refers to his previous patent of April 30th, 1859, producing purples by mixing aniline red and aniline blue, use of nitrate of manganese and chloride of antimony for producing red colours. No. 67.
- 1861, January 12th.—Girard: Production of blue and purple colours by heating together aniline red colour and aniline oil. No. 97.
- 1861, February 8th.—Stark: Obtaining colours by acting upon aniline with cyanides; afterwards, by disclaimer, the claim was confined to yellow prussiate of potash. No. 316.
- 1861, February 22nd.—Martin: Acting upon aniline with nitrate of lead and other nitrates in conjunction with glacial acetic acid. No. 456.
- 1861, August 10th.—Newton, from Meister, Lucius, and Co.: Production of blue and violet colours by heating rosaniline with caustic soda and then with benzoic acid and toluidine. No. 1,972.
- 1862, January 20th.—Nicholson: Production of purple colour by heating aniline red alone and without admixture of aniline. No. 147.
- 1862, January 29th.—Williams: Aniline colours from aniline and phosphate or acetate of mercury, also by heating a salt of

- aniline with uncombined aniline and arsenious acid. No. 271.
- 1862, June 12th.—Ingham and Wood: Purple colours from aniline red and alkalies, organic or inorganic (except aniline), by heating with caustic soda and lime. No. 1,746.
- 1862, June 24th.—Nicholson: aniline blue soluble in water obtained by heating ordinary aniline blue with four times its weight of concentrated sulphuric acid to 300° F. No. 1,857.
- 1862, July 3.—Gilbee: Production of aniline blue from aniline red by heating it with caustic soda or with acetate of aniline, also treating the crude blue successively with weak and strong sulphuric acid. No. 1,939.
- 1862, July 28th.—Spence, from Guinon, Marnas, and Bonnet: Production of a blue colouring matter called azuline by heating peonine with aniline, or subsequently purifying the product. No. 2,132.
- 1862, August 14th.—Blockey: Colours produced by acting upon aniline with nitric and hydrochloric acids. No. 2295.
- 1862, September 4th.—Clark, from Collin: Blue colour obtained by heating aniline red with crystallized toluidine. No. 2,446.
- 1862, September 17th.—Watson: Colours obtained by treating aniline with aqua regia. No. 2,552.
- 1862, October 8th.—Clavel: Making aniline violets soluble in water by treatment of them with cold Nordhausen vitriol, or hot English vitriol, the former being preferred. No. 2,718.
- 1862, November 2nd.—Smith: Red colours produced by heating aniline with nitric acid and arsenious acid. No. 3,044.
- 1862, December 10th.—Price, from Eisenlohr: Aniline blue produced by heating salts of aniline (of organic acids) with fuchsine and purifying the product. No. 3,312.
- 1862, December 18th.—Wilson and Manning: Colours obtained by passing chlorine through a mixture of aniline and bichloride of arsenic. No. 3,387.
- 1863, January 8th.—Monteith: Colours made from aniline by simply heating the muriate and sulphate with free aniline

- and sand, or other mineral substances in a similar physical condition. No. 70.
- 1863, January 12th.—Dawson: Red colours by treating with arsenic acid and water (about 23 per cent. water) in an iron cylinder under pressure. No. 92.
- 1863, January 12th.—Usebe: Production of aniline green from rosaniline, aldehyde, and hyposulphites. No. 97.
- 1863, January 15th.—Williams: Red colour by boiling a salt of aniline with acetate of mercury. No. 138.
- 1863, February 26th.—Price, from Ersonrohr: Blue colours from mixtures of aniline and rosaniline, with benzoates or acetates of soda or ammonia. No. 541.
- 1863, March 11th.—Monteith: Brown and Havanna colours from rosaniline and dry salts of aniline, the hydrochlorate alone being suitable. No. 660.
- 1863, March 14th.—Boaler: Colours obtained by acting upon aniline with nitrous gases. No. 700.
- 1863, March 17th.—Delaire, from Girard: Brown colours obtained by acting upon aniline red with hydrochlorate of aniline, similar to patent of March 11th, above. No. 717.
- 1863, April 24th.—Passavant: Aniline blue colours obtained by acting upon rosaniline with aniline and acetate of soda. No. 1,021.
- 1863, April 25th.—Porrier and Chappat: Blue and violet colours obtained by heating rosaniline with naphthaline, with or without benzoic acid. No. 1,036.
- 1863, May 7th.—Holliday: Blue colours by heating aniline, rosaniline, and benzoic acid together. No. 1,148.
- 1863, May 9th.—Williams: Blue colour from rosaniline salts and oleate of aniline, or 1 part rosaniline, 4 parts oleic acid, and 4 parts aniline. No. 1,173.
- 1863, May 22nd.—Hoffmann: Purple colours from rosaniline and the iodites or bromides of the alcohol radicals, as ethyl, methyl, etc., heated together under pressure. No. 1,291.
- 1863, July 9th.—Wilson: Red colours obtained by the action of nitric acid and gradual addition of peroxide of manganese. No. 1,713.
- 1863, November 5th.—Smith: Colours obtained by action of sali-

- cyclic acid and aniline upon aniline purple; also carboic acid with magenta. No. 2,739.
- 1863, November 6th.—Perkin: Modification of the mauve colour by heating it with iodide of ethyl to obtain bluer and redder shades. No. 2,762.
- 1863, November 11th.—Dawson: Modified shades obtained by heating rosaniline with iodide of allyl. No. 2,803.
- 1863, November 18th.—Nicholson: Treating salts of rosaniline with iodides or bromides of the alcohol radicals. Compare Hoffmann's patent of May 22nd, 1863. No. 2,892.
- 1863, November 18th.—Hirzell: Colours obtained by treating rosaniline with aldehyde and acids, and afterwards with sulphide of ammonium. No. 2,894.
- 1863, December 5th.—Wanklyn, from Lucius: Orange and yellow colours from residues of red dyes by treatment with nitric acid. No. 3,063.
- 1863, December 30th.—Phillips: Purple colour by treating sulphate of aniline with sulphate of iron and hypochlorite of lime. No. 3,302.
- 1863, December 31st.—Dale and Caro: Yellow colours by treating aniline salts with alkaline nitrites; brown colours from phenylindiamine and toluylindiamine by same treatment. No. 3,307.
- 1864, February 3rd.—Watson: Blue colours by heating rosaniline with aniline and lac or other resins. No. 286.
- 1864, February 8th, Laurent and Casthelaz: Violet colours by making a fluosilicate of aniline and acting upon it with bichromate. No. 329.
- 1864, March 4th.—Brooman, from Bredt: Green colour by means of aldehyde and hyposulphites. No. 549.
- 1864, April 20th.—Levinstein: Purple, blue, and violet colours by heating rosaniline with nitric ether. No. 981.
- 1864, May 10th.—Wanklyn: purple by treating rosaniline with a liquid obtained by boiling mannite with hydroiodic acid, sp. gr. 1.7, and phosphorous. No. 1,181.
- 1864, May 12th.—Sachs, from Froehling: Blue colours obtained by treating rosaniline with aniline oil and dry soap or stearate of soda. No. 1,199.

- 1864, May 18th.—Smith : Violet colour obtained by heating salts of rosaniline with iodide or bromide of an alcohol radical. No. 1,252.
- 1864, June 20th.—Smith and Sieberg : Violet colours obtained by heating rosaniline with hydriodic acid and alcohol. No. 1,525.
- 1864, July 5th.—Philips : Purple and blue colours by treating aniline with arsenic and protosulphate of iron, or by treating rosaniline with protosulphate of iron. No. 1,669.
- 1864, July 26th.—Dalzell : Colours obtained by acting upon rosaniline by iodoform or bromoform. No. 1,867.
- 1864, August 1st.—Carter : Green colour by action of sulphate of copper and oxalic acid upon aniline, and mixing with blue or purple. No. 1,913.
- 1864, August 9th.—Pflughaupt : Red produced by oxidation of salts of aniline by hot air. No. 1,949.
- 1864, August 10th.—Lowe : Colours produced by long-continued boiling together of aniline and picric acids. No. 1,994.
- 1864, August 19th.—Parkes : Colours obtained by acting upon aniline with chloride of sulphur or chloride of carbon. No. 2,060.
- 1864, September 6th.—Perkin : Violet colours from rosaniline by action of the compound produced by treating bromine and turpentine together. No. 2,181.
- 1864, September 14th.—Johnson, from Gaultier de Claubry : Substitution of soap worts, Panama bark, or other gelatinous fluids as solvents, instead of alcohol. No. 2,244.
- 1864, November 19th.—Wilson and Wanklyn : Purple colours obtained by treating rosaniline with nitrate of methyl. No. 2,894.
- 1864, November 22nd.—Durand : Yellow or orange colour by treating aniline red with zinc powder. No. 2,916.
- 1865, March 13th.—Wise, from Levinstein : Orange and brown colours by treating rosaniline with formic acid and acetate of soda. No. 705.
- 1865, April 20th.—Smith and Sieberg : Violet colours by treating rosaniline with iodides of the radical of acetone. No. 1,098.

- 1865, August 9th.—Schad: Colours obtained by treating rosaniline with iodide of ethylene in alcoholic solution. No. 2,070.
- 1865, August 26th.—Wanklyn: Violet colours obtained by action of iodide of isopropyl upon rosaniline. No. 2,194.
- 1865, September 22nd.—Schultz: Treating rosaniline with hypnitric acid, also treating printed colours with the same to fasten. No. 2,424.
- 1865, October 3rd.—Brooman, from Chevalier: Red and purple colours by treating arseniate of aniline with nitrates. No. 2,536.
- 1865, October 6th.—Holliday: Violet and blue colours by treating a salt of aniline with nitro-benzole and heating, afterwards purifying. A red colour also from the same treatment. No. 2,564.
- 1865, November 2nd.—Schad: Colours produced from rosaniline with aniline and salts of quinine. Also for treating ethylene violet (see 1865, August 9th) with aniline to produce other shades. No. 2,825.
- 1865, December 4th.—Paraf: Obtaining scarlets by treating rosaniline with nitrous gas or with nitrites and acids. No. 3,111.
- 1865, December 29th.—Hughes, from Lauth: Green from aniline by first making a blue by means of aldehyde, and changing it by mixture with polysulphides or substances yielding nascent sulphur. No. 3,374.
- 1866, February 3rd.—Holliday: Red colours by treating salts of aniline with nitro-naphthaline. No. 341.
- 1866, March 10th.—Philips: Blue and purple colours obtained by acting upon rosaniline with acetates of lead or baryta and aniline. No. 732.
- 1866, March 17th.—Dancer: Colours obtained by acting upon rosaniline with aldehyde, precipitating by lime or soda, and dissolving in acetic acid. No. 793.
- 1866, March 28th.—Jaeger: Yellow produced by acting upon chloride of aniline with nitrate of mercury. No. 904.
- 1866, April 2nd.—Guétat: Violet and blue colours by adding 10 per cent. of benzoic acid to aniline. No. 938.
- 1866, April 5th.—Jaeger: Red colour produced by acting upon

- aniline with the yellow body mentioned in his patent of 1866, March 28th. No. 968.
- 1866, April 18th.—Girard and de Laire: Blue colours by first preparing diphenylamine by acting upon chloride of aniline with aniline under pressure, and subsequently treating this with sesqui-chloride of carbon. No. 1,093.
- 1866, April 19th.—Nicholson: Blue colour obtained by treating regina purple with aniline and heat; to make it soluble refers to patent 1,862, June 24th (No. 1,857). No. 1107.
- 1866, May 10th.—Holliday: Improvements in purifying green and blue colours obtained from rosaniline by the iodides of the alcohol radicals. No. 1,340.
- 1866, July 23rd.—Bousefield: Colours made from the alcohol radicals, aniline salts and bichloride of tin. No. 1,912.
- 1866, August 14th.—Wanklyn and Paraf: Converting violets into greens by liberating the bases and treating them with iodide of ethyl and alcohol. No. 2,083.
- 1866, August 22nd.—Caro: Production of colours by treating rosaniline with nitrous acid, and submitting the azo-compound to the action of chloride of tin and other reducing agents. No. 2,153.
- 1866, October 16th.—Bousefield: Producing green and blue colours from violet by action of iodide of methyl with methylene and sulphuric acid; and for acting upon rosaniline with the same reagents. No. 2,669.
- 1866, November 6th.—Grote: For treating certain aniline greens with sulphurous acid to make them more permanent when applied as steam colours. No. 2,872.
- 1866, December 5th.—Brooman, from Lauth: Obtaining violet colours by acting upon methylaniline and dimethylaniline with hydrochloric acid, or by acting upon them with chloride or nitrate of copper, or acetate of mercury. No. 3,195.
- 1866, December 18th.—Schad: Reducing aniline violet colours to very fine powder by melting them with chloride of aniline and then treating with water, so that they may be used without alcohol. No. 3,326.
- 1867, May 15th.—Smith: Colours obtained by acting upon rosaniline with chloride of mesityl, or chloropropylene and

- methyated spirit and lime ; also by using the bromine derivatives of oil obtained by distilling gutta-percha. No. 1,433.
- 1867, August 6th.—Luthringer : Acting upon rosaniline with bi-oxide of barium and sulphuric acid, or with oxygenated water, producing the colour called geranosine. No. 2,270.
- 1868, May 1st.—Abel, from Bloch : Aniline grey produced by acting upon aniline with arsenic acid at 75°. Five drops dye a hank of wool. No. 1,424.
- 1868, June 22.—Johnson, from Durand : Red colour obtained by acting upon aniline with arsenic acid and nitrite of soda. No. 2,017.
- 1868, September 4th.—Johnson, from Zweifel : Blue colour by acting upon aniline with chlorate of potash, sulphate of iron, and salammoniac. No. 2,725.
- 1869, September 28th.—Abel, a communication : Green from benzyl-aniline and analogous bodies which eliminate hydrogen. No. 2,818.
- 1870, April 22nd.—Bardy and Dusart : A general chemical process for applying the polybasic acids with phenoles to produce new alkaloids. No. 1,172.
- 1870, May 18th.—Casthelaz : Improved methods of extracting aniline and preparing its salts. No. 1,425.
- 1872, October 11th.—Nicholson : Separation of rosaniline from other bases by its greater solubility in superheated water. No. 3,007.
- 1872, October 19th.—Nicholson : For making magenta without arsenic acid by heating together aniline, nitric and hydrochloric acids in suitable vessels to a temperature of 350° or 400° F. No. 3,094.
- 1872, October 19th.—Price : Details in the manipulation of magenta by which the arsenic may be recovered for using again. No. 3,095.
- 1873, December 24th.—Casthelaz : For treating aniline with sulphuric acid and bichromate of potash and heating. No. 4,225.
- 1875, March 20th.—Versmann : For extracting phosphine from the crude aniline dye by means of bisulphide of carbon or petroleum. No. 1,038.

- 1875, July 5th.—Wolff and Betley : Blue colours from a mixture of aniline and nitro-benzol acted upon by protochloride of tin. No. 2,421.
- 1875, July 5th.—Wolff and Ascroft : For recovering aniline from wash waters by means of sulphate of copper, and using the same for printing. No. 2,422.
- 1876, January 20th.—Levenstein : Extracting colouring matter from the residues of the magenta melt. No. 238.
- 1876, January 26th.—Wolff and Bettley : Colours from aniline, with or without toluidine, by means of hydrochloric acid and chlorine, with iodine and bromine, or peroxide of manganese, nitric acid, chromic acid, &c. No. 313.
- 1876, December 1st.—Butler : Preparation of aniline colours by means of muriatic acid and chlorate of potash. No. 4,655.
- 1876, December 14th.—Girard and others : Preparing aureosine from any of the phenols by means of diatomic acids and hypochlorites, &c. No. 4,839.
- 1876, December 20th.—Wilson and Cant : Exhaustion and separation of yellow colouring matters from crude rosaniline, and purifying the latter. No. 4,912.

The following patents refer mainly to the fixing or applying the aniline colours upon fibrous matters ; some of them have been previously referred to in other parts of this work :—

- 1858, December 29th.—Kay : For the use of albumen, protein, lactarine, caseine, and similar substances, along with aniline colours. No. 2,976.
- 1859, May 21st.—Perkin and Gray : Lead as a mordant for aniline colours by printing the acetate, and fixing by means of carbonate of soda and caustic ammonia. No. 1,257.
- 1859, May 23rd.—Crum : Gluten in alkaline solution to be used as a substitute for albumen. No. 1,263.
- 1859, May 28th.—Crum : Use of preparations of gluten without alkali ; also, of lactarine and caseine when used as a mordant. No. 1,319.
- 1859, October 18th.—Rott : Gluten prepared by acids as a substi-

- tute for albumen in the application of aniline colours. No. 2,385.
- 1859, December 10th.—Calvert and Lowe: Use of a mordant, consisting of tannin matter and alumina as a substitute for albumen and lactarine. No. 2,801.
- 1860, March 12th.—Gratrix: The cloth prepared with stannates and then passed through tannin. No. 612.
- 1860, September 12th.—Gratrix and Javal: Use of tannin in various ways to fix the aniline colours upon cotton goods. No. 2,205.
- 1860, September 27th.—Mennons, from Guignon: Cotton goods are prepared with emulsion of oil and soda mixed with cow dung. No. 2,345.
- 1860, October 8th.—Hughes, from Depouilly and Lauth: The use of tannin to form precipitates and lakes, and their application as pigments. No. 2,432.
- 1860, November 6th.—Smith: Precipitating the colouring matter of magenta upon a mixture of starch and alumina, or other earth, to make lakes suitable for printing. No. 2,729.
- 1861, March 14th.—Pattison: Tannin mixed with magnesia or alkaline earths, and the aniline colours added for printing. No. 627.
- 1861, March 18th.—Miller: Use of tannin from galls with stannates of the alkalies neutralized with tartaric acid. No. 682.
- 1861, March 20th.—Brooks: Method of combining aniline colours with madder or garancine colours by means of tin and tannin. No. 693.
- 1861, March 20th.—Lloyd and Dale: Use of tartarized antimony to fix the aniline colours printed in mixture with tannin. No. 701.
- 1861, April 4th.—Miller: Appears not to differ from the same patentee's method 1861, March 18th. No. 835.
- 1861, May 1st.—Pattison: The colours are to be fixed by alkaline earths or their salts without tannin; acetate of lime is given as an example. No. 1,092.
- 1862, July 24th.—Perkin, from Schultz: Use of arsenite of soda along with acetate of alumina for fixing the colours by steaming. No. 2,107.

- 1863, January 21st.—Caro and Dale :—Use of acroleine to change the hue of aniline colours when fixed upon cloth. No. 192.
- 1863, June 11th.—Schlumberger : Aniline colours precipitated by borate, silicate, or phosphate of soda dissolved in suitable solvents and applied without tannin. No. 1,458.
- 1864, September 30th.—Brooman, from Poirrier : Dissolving or suspending aniline colours in solution of soap worts instead of alcohol. No. 2,411.
- 1865, May 25th.—Maxwell : Preparation of the cloth by oily or soapy bodies, emulsion of soda and oil, etc. No. 1,428.
- 1856, June 19th.—Paraf : Use of the glycerine solution of arsenious acid for mixing with acetate of alumina to form a mordant for aniline colours. No. 1,642.
- 1816, August 17th.—Paraf : Use of the glycerine solution of arsenious acid called arsenious glyceric ether to fix aniline colours without alumina. No. 2,115.
- 1868, February 14th.—Bonneville, from Zinsmann : Suspension or solution of aniline colours in glue and acetic acid, gums, glycerine, or soap wort to fit them for dyeing. No. 496.
- 1869, February 10th.—Clayton : Use of a mixture of kid glue, turpentine, water, and blood albumen for fixing aniline colours. No. 420.
- 1869, March 4th.—Johnson, from Blumer-Zweifel : A method of treating aniline blue colours upon cloth so as to improve them. No. 664.
- 1873, March 3rd.—Hunt : Use of the less soluble part of catechu for fixing aniline colours. No. 766.

The number of patents and the varieties of processes included in the preceding lists illustrate very well the amount of attention which has been paid to the remarkable series of colours obtained from aniline, and all within a period of twenty years. It is perhaps yet too soon to attempt to make a complete estimate of what influence these colours have had upon the arts of dyeing and printing, but sufficient

time has elapsed to demonstrate that for the purposes of the cotton dyer and printer there is no single colour from aniline, except Lightfoot's black, which possesses even a moderate degree of permanency, and that out of the vast number of artificial colouring matters which are or have been in trade there are none, excepting alizarine, which he can use with safety and security, or without fear of having some day to find his reputation and his profits diminished in consequence. In the silk and woollen trade the circumstances are different; upon these fibres the aniline colours have as much permanency as most of the fancy colours which were in use previous to their discovery, and possess great advantages over the older colours upon the score of brilliancy of hue and facility of application. In the case of artificial alizarine, we have seen that an ancient and valued dyestuff, madder, has been almost banished from the market by its young rival; but it cannot be shown that the consumption of any single dyestuff has been diminished in consequence of the use of the aniline colours, or that their market value has been reduced to an appreciable extent; that is to say, in other words, that none of the aniline colours have been found efficient substitutes for the well-known natural dyestuffs. They are an entirely new class of colouring matters, and have hardly interfered with the old ones.

For application of aniline colours in calico printing the processes are practically reduced to either albumen (or lactarine), the arsenical alumina mordant, or

tannin matters. Albumen is safest in the extract or pigment styles when the quantity of colour in the design is not large; the alumina mordant with arsenic is probably preferable in massive objects, or in a ground or cover. The only aniline colour of general application by the latter method is the mauve or purple, other aniline colours are only employed in the lower class of prints, being very unstable; at present aniline green fixed by tannin is in use.

In cotton dyeing, a tannin mordant combined usually with tin and alumina is most generally used; fatty matters are sometimes employed, as previously referred to.

In woollen and silk dyeing the method of application of the aniline colours is of the greatest simplicity; no mordant is required for the majority, and the workman has no more to do than work the properly bleached material in a solution of the colouring matter at the temperature found most convenient.

I do not attempt to give in this place even the names of the numerous aniline dyes which flood the markets of the world. Scarcely a month passes without the introduction of some new product or a new name. Many much vaunted dyes have already vanished, and it may be safely predicted that most of those which are now current will also quietly disappear within a short time, leaving behind a few standard preparations from which all the desired shades may be obtained. When this happens it will be time to write a history of the aniline colours.

Aniline Black.—The black derived from aniline has no resemblance in its properties, manner of production, or application to any other of the aniline colours. They are manufactured articles supplied to the consumer ready prepared, this has to be made upon the cloth itself. They are all characterised by want of stability; this is one of the most permanent colours which it is possible to conceive. Its history can in great measure be read in the successive patents granted for its preparation and application, and as these only commence in 1863, I give a list of the most important of them. There is an earlier patent not included, dated September 27th, 1860, to Calvert and others, for obtaining a dark green and a blue colour from aniline and chlorate of potash, this colour they called *emeraldine*; it never came into use, but was undoubtedly an imperfect aniline black, and really differed from it only in the absence of copper and deficiency of concentration. These inventors never found out until too late that the tantalising promises of their discovery were owing to the use of copper rollers and copper vessels, which unknown to them yielded up to the solutions sufficient metal to sometimes give a good result, but one not to be depended upon, and the process was given up.

1863, January 17th.—Lightfoot: The use of starch paste, chlorate of potash, aniline, muriatic acid, perchloride of copper, and salammoniac. In the complete specification, but not in the provisional, is mentioned padding of the cloth with copper

- salts and the use of red prussiate with oxalic acid to make a steam aniline black. No. 151.
- 1863, February 25th.—Gatty : Padding the cloth with acetate of alumina and bichromate of potash, and printing on muriate of aniline—cloth to be dyed red afterwards—on Turkey red to pad with neutral chromate of potash. No. 517.
- 1863, December 4th.—Hughes, from Cordillot : Aniline black from aniline salt, chlorate of potash, and red prussiate of potash. No. 3,045.
- 1864, June 7th.—Hughes, from Lauth : The use of sulphide of copper instead of soluble salts of copper with chlorate of potash.*
- 1865, March 22nd.—Paraf : The use of fluosilicic acid with salts of aniline and chlorate of potash, so as to avoid the use of copper. No. 804.
- 1865, August 8th.—Buchanan and Boyd : Depositing insoluble salts of copper on the cotton, and printing aniline salt without oxidising agents. No. 2053.
- 1865, September 11th.—Lightfoot : Aniline black applied to wool and other animal fibres, by previously treating the fibres with chloride of lime, so as to oxidize them. No. 2,327.
- 1865, November 6th.—Paraf : The use of other chlorates more soluble than chlorate of potash ; mentions those of soda, baryta, and lead ; in provisional specification speaks of exposing the goods to ammonia gas before dunging. No. 2,859.
- 1866, March 27th.—Higgins : The use of several chemical mixtures which are said to give rise to chromic acid upon the cloth. No. 897.
- 1866, April 26th.—Paraf : The use of some compounds of chromium, said to give rise to chromic acid upon the cloth. Much similarity to the preceding patent. No. 1174.
- 1867, October 9th.—Thomas, from Persoz : The use of bichromate of potash and other chromium compounds for dyeing aniline black upon wool and cotton. No. 2843.
- 1867, December 24th.—Clark, from Coupier : Production of aniline black pigment by heating together aniline, nitrobenzol,

* In the specification misprinted "chromate of potash."

- hydrochloric acid, and iron filings, with a little copper. No. 3,657.
- 1868, July 27th.—Higgin: The production of a quite neutral chloride of aniline by adding aniline oil to metallic chlorides, such as chloride of chromium or perchloride of iron, and the use of disulphocyanide of copper instead of sulphide of copper. No. 2,351.
- 1868, December 5th.—Francillon: Dyeing of fur and hair with aniline black by nearly the same materials as used for cotton. No. 3,700.
- 1869, May 10th.—Lauth: Preparation of cloth to be dyed by depositing upon it peroxide of manganese either from permanganate or from manganese salts; requires simply dipping in solution of aniline. No. 1,421.
- 1870, June 30th.—Pinkney: Use of nickel salts to replace copper salts in aniline black. No. 1,863.
- 1870, October 12th.—Lightfoot: For making chlorate of soda and chlorate of ammonia for aniline black by decomposition of chlorate of potash with tartrates. No. 2,692.
- 1871, October 16th.—Pinkney: The use of salts of uranium and vanadium for aniline black, with or without nickel. No. 2,745.
- 1872, June 6th.—Morgan-Brown: For an apparatus for dyeing aniline blacks, being a closed cylinder kept revolving and heated up to the required temperature. No. 1,710.
- 1872, June 10th.—Casthelaz: A black obtained by acting upon aniline with bichromate of potash. No. 2,009.
- 1874, December 24th.—Selton and Pinkney: Refers to vanadium to be also used for other colouring matters. No. 4,433.
- 1875, May 1st.—Clark, from Grawitz: Production of aniline black by the action of certain metallic salts and chromates. No. 1,620.
- 1876, September 25th.—Orr: Treatment of the developed black by hot chromate solutions to prevent subsequent greening. No. 3,731.
- 1876, November 9th.—Dreyfus: Preventing the greening of aniline blacks by passing them through a solution of aniline violet. No. 4,340.

The discovery of aniline black is entirely due to the late Mr. John Lightfoot, of Accrington, Lancashire. It was known to him in the year 1860, and resulted from experiments he was making upon what was called "oil of naphtha," actually an impure aniline. He shewed specimens of it to his friends in 1860. I saw some bits of calico with aniline black from him in 1861, printed with the finger. Why he let it rest until 1863 without patenting is not known. The Swiss and French printers were the first to take it up with vigour, and Mr. Lightfoot states that 50,000 pieces were printed with his original colour in a short time; but this was by block printing, for it was found impossible to use it in the printing machine on account of the strongly corrosive action of the colour upon the doctor; not more than 50 or 100 yards could be printed without filing up, and whetting the doctor afresh. Cordillot's colour, next in date, in which red prussiate replaced copper salts, was not open to this objection, but it was much more costly, and did not keep well. Various devices of preparing the cloth with copper and with chlorates were tried, but found impracticable, and at this time (1863) it seemed likely that the trade would have to relinquish the application of the finest and most promising colour which had appeared for at least half a century. The discovery of Lauth, in 1864, that the insoluble precipitate of copper produced by adding a solution of sulphur in soda to sulphate of copper (commonly called sulphide of copper) could perfectly

replace solution of copper, at once removed all difficulties in the printing of aniline black, and since that time it has been generally and largely used by the whole trade. Lightfoot was well aware that copper was not the only metal which could induce the formation of the black, and in his earliest patent he mentions iron and antimony, and in later patents vanadium and other metals. In published documents he distinguished vanadium as being the most active of thirty or forty different metals which he had tried. Probably he paid no more attention to vanadium, regarding its action only as a point of scientific interest, because it was a great rarity and obtainable only at such a price as entirely excluded it from technical use. About this time vanadium had been discovered at Mottram St. Andrews, in Cheshire, and Dr. Roscoe had availed himself of supplies obtained from this source to have its compounds produced for him in comparatively large quantities for his scientific researches, the raw ore afterwards passed into the hands of the Magnesium Metal Company, of Manchester, and they extracted the vanadium as vanadic acid or oxide, and their agents offered it for sale at three guineas per ounce about the end of 1870. Pinkney patented the use of this metal on October 16th, 1871, and used it for making an aniline marking ink, which was very successful; but it does not appear that any move was made to apply vanadium for aniline black in calico printing until 1875, when experiments were privately made at several printworks

in Lancashire with it, and a considerable number of pieces printed with more or less success. Attention was, however, strongly called to the matter by a paper which appeared on January 20th, 1876, in the Bulletin of the Chemical Society of Paris, written by Guyard, and since that time it has been well discussed in the scientific and technical journals.* Vanadium does not differ from copper in its ultimate action upon the mixture of aniline, salt, and chlorate; it is remarkable for the very small quantity required to develop the black. Mr. Witz states that he works with about one-tenth part of a grain of vanadium (reckoned as metal) per gallon of colour, and that it is not well to exceed that proportion; other practical colourists consider that this quantity should be increased considerably to be safe—say to about five grains of the chloride of vanadium, or the vanadate of ammonia per gallon of colour.

At the present time Lauth's colour, with sulphide of copper, is the one chiefly in use, though many colourists prefer the vanadium salts and use them exclusively. Cordillot's red prussiate colour is still sometimes used in conjunction with steam colours, as it is less likely to injure the strength of the cloth. Chlorate of potash has in general been substituted by the chlorate of soda, which is more soluble in water. When printed the aniline black composition is nearly colourless; when hung up in warm and moist air it

* *Textile Colourist*, i., pp. 127, 196, 284; ii., pp. 13, 171, etc. Witz, in *Bull. de Rouen*, iv., p. 340.

speedily assumes a dark olive green colour ; it is then fixed, and may be washed off in water, or passed through weak solution of soda ash or bichromate of potash.

The application of aniline black has given in the past much trouble to colour mixers and printers; but, at the present time, the conditions necessary for success are better understood, which, together with the supply of purer and more regular qualities of aniline salt, enables the colour to be worked without special difficulties. The former inconveniences of this colour, excluding the printing, were mainly two—viz., failure of the development into black, and tendering of the cloth. In the first case the colour upon ageing only became grey, or drab, and could not be made black; this was nearly always a fault of the colour mixture, and might arise from various causes, generally blunders or negligence, or using up old colours which were either spoiled by being kept in a warm place, or by being dirtied with other colours containing acetates. The ageing may be sometimes in fault; it should be progressive, without checks from falling of temperature in the night time—the sooner the goods are hung up after printing the better for them. The tendering of cloth, which sometimes occurred, was no doubt owing to the chlorates and the acid salts of aniline, generating free chlorine compounds, more rapidly than they could be absorbed or neutralised by the aniline itself. Over drying or under drying on the printing machine are

both likely to tender the cloth, the former by heating the colour too strongly, the second by leaving the colour in a warm and moist state in which the elements react upon one another rapidly, developing corrosive gases;—instances are reported of under dried aniline blacks heating and bursting into flame upon lying in a heap for a short time. Thin and watery colours, made from bad starch, are likely to tender the cloth, owing to the separation of the liquor and thickening. Aniline black should be worked at a medium thickness, and made with good sound starch, strengthened, if necessary, by tragacanth or a little British gum, and care should be taken that in working stripes, checks, or continuous lines of any sort, that the colour is not too thin, for it is in these engravings that tenderness or weakness of the cloth is most injurious. The bad working of the sulphate of copper colour, sometimes complained of, I do not understand. I always found it to work as well as any other paste colour, printing 1,200 to 1,400 yards without stopping.

The chemical composition of aniline black is not yet known with certainty, and the theory of its production is consequently obscure; it appears, however, to be proved that the essential materials for its production in calico printing are certain chlorinated compounds which can be evolved from chlorate of potash or other chlorates. Neither copper, vanadium, nor any other metal remains in the finished black; these metals only act in facilitating the decomposition of the chlorates employed. How they act is not

known, and that they should act so powerfully in such minute or almost infinitesimal quantities is a matter of astonishment to all who are intimately acquainted with the phenomena which takes place.*

Greening of Aniline Black.—The only colour which comes near to aniline black in fastness is indigo blue, and that valuable colour is weak in some points where the aniline black is strong. No other black known to dyers or printers is at all comparable with it; it resists all the agents in use on a dye-works, and can support without injury dyeing operations, and treatments with acids, alkalies, and bleaching powder. But soon after it came into extensive use it spontaneously developed a weak point which materially reduced its value. In certain situations where it came into contact with slightly acid vapours, and especially sulphurous acid, arising from the burning of coal and coal gas, it was found to lose its beauty and acquire a dull greenish hue, making it flat and disagreeable to the eye. This change was found to be a superficial or transient one, for the black colour was restored to its original depth and purity by washing in soap or alkalies; but the colour was always liable to the same deterioration when exposed again to the same influences. All kinds of aniline black were subject to this greening, those which were most dense resisting the longest or

* See Rosenstiehl on Theory of Aniline Black, *Textile Colourist*, i., p. 294, from *Bull. de la Soc. Ch. de Paris*, xxv., p. 356. Further references are given in a classified form in another place.

shewing it the least. A remedy for this defect was discovered by M. Jeanmaire, of Koechlin Brothers, in 1876.* It consists in treating the usual black colour after its development with certain oxidizing agents—that which is recommended for single blacks being a weak solution of persulphate of iron heated up to about 170° or 180° F., the goods being kept in the liquid for half an hour. In cases where an iron salt would be objectionable other oxidizing agents may be used, as chromic acid, some of the chlorates, as chlorate of alumina, nitrites, or sulphonitrous acid. Blacks thus treated are completely invulnerable to greening influences, possessing their other characters unchanged.†

Naphthaline Colours.—Strong hopes have been entertained that naphthaline, or its immediate derivatives, would yield some useful and permanent colours for dyeing and printing. Up to the present time these hopes have not been realized. The best recent attempts in this direction may be found described in a paper of MM. Rhem and Lamy.‡ Certain shades of grey and chocolate possessing a fair degree of stability have been produced, but they have no special point to recommend them as substitutes for existing colours. I do not propose to go into any details concerning this class of colours. For purposes of reference I

* *Moniteur Scientifique* (3), vii., p. 81. *Textile Colourist*, iii., pp. 18, 20.

† See a paper by Witz, *Bull. de Rouen*, v., p. 238. *Textile Colourist*, iv., p. 109; also Orr's patent, *Textile Colourist*, iii., p. 303.

‡ *Bull. de la Soc. Ind. de Rouen*, iv., p. 29. *Textile Colourist*, ii., pp. 1, 4.

append a list of the more important patents referring to them, including not only those from naphthaline, but other of the coal-tar products not coming under the head of aniline.

- 1860, October 4th.—Cowper, from Battalier : A red orange colouring matter obtained from the latter products of the distillation of pitch. These products are soluble in sulphuric acid, and the solution neutralized with chalk forms the dye. No. 2,401.
- 1860, October 12th.—Johnson, from Frost : Violet colour obtained by the action of nitric acid upon naphthaline, followed by treatment with alkaline sulphurets. No. 2,492.
- 1861, January 5th.—Vial : Colouring matters obtained from coal-tar products and waste gas lime by means of alkalis and oxidation by air. No. 27.
- 1861, January 14th.—Hall : Colours from heavy oil of coal-tar and dead oil by reducing the nitro-compounds with sulphites, iron filings, etc. No. 101.
- 1861, May 1st.—Roussin : Colours obtained upon fabrics by dipping them in a solution of hydrochlorate of naphthaline and then into a solution of nitrite of potash ; red shades obtained. No. 1,087.
- 1861, July 29th.—Scott : Red and violet colours by acting upon binitronaphthaline with sulphuric acid and deoxidizing by zinc, sulphurous acid, etc. No. 1,893.
- 1861, December 24th.—Casthelaz : Colouring matters obtained by acting upon nitrobenzine with reducing agents so as to avoid production of aniline. No. 3,225.
- 1862, July 28th.—Spence, from Guignon and others : A red colour called peonine, obtained from phenic or carboic acid by acting upon it with oxalic and sulphuric acid. No. 2,130.
- 1862, December 23rd.—Brooman, from Chalamel : A ruby colouring matter by mixing coralline and fuchsine. No. 3,423.
- 1863, March 30th.—Newton : A yellow colour for dyeing silk and wool from naphthaline by treating it with nitric acid. No. 821.

- 1863, August 6th.—Lowe : Employment of phosphates, arsenates, and borates with aurine or rosolic acid to make this colour more soluble in dyeing baths. No. 1,936.
- 1864, June 21st.—Martius : Black, drab, and brown colours from phenylendiamine and naphthylendiamine by printing these substances and exposing them to the action of air and ammonia. No. 1,540.
- 1864, November 9th.—Dale and others : Treatment of nitrate of naphthylamine with mixture of nitric acid and nitrite of soda to produce a yellow colouring matter called chrysonaphthylic acid. No. 2,785.
- 1865, June 13th.—Laurant and Casthelaz : Improvements in preparing chloroxynaphthalic acid and phthalic acid for use in printing. No. 1,605.
- 1866, October 17th.—Girard and Laire : Blue colours from diphenylamine by treating with sesquichloride of carbon and heating ; also by treating with oxalic acid. No. 2,686.
- 1866, November 30th.—Clark, from Schlumberger : Green colour from toluidine red by treating with sulphuric acid, aldehyde, and hyposulphites. No. 3,152.
- 1867, January 29th.—Nève : A scarlet resembling cochineal from rosolic acid by treating it with alkalies. No. 242.
- 1868, January 22nd.—Clavel : Red colours by acting with nitrate of mercury upon compounds obtained by the distillation of naphthylamine. No. 225.
- 1868, July 22nd.—Johnson, from Clavel : Red colour obtained by acting upon naphthylamine and isomeric bodies with acetic acid and nitrate of soda. No. 2,296.
- 1869, January 12th.—Price, from Darmstädter and Wichelan : Yellow dyeing matters by acting upon naphthaline so as to produce dinitronaphthylic alcohol, which can be used in dyeing and printing. No. 89.
- 1869, July 20th.—Johnson, from Blumer Zweifel : Grey and violet colours by printing a mixture of chloride of naphthylamine and chloride of copper. No. 2,196.
- 1869, November 29th.—Reissig : Brown colours from carbolic acid by converting it into diamidophenylic acid, which rapidly oxidizes in the air. No. 3,451.

- 1870, February 9th.—Bardy : Blue and other colours obtained by acting upon a new base called methyldiphenylamine by acting upon it with substances capable of eliminating hydrogen. No. 376.
- 1872, April 12th.—Lamy : Chocolate and garnet colours from naphthylamine and its derivatives. No. 1,091.
- 1873, March 20th.—Newton : Making colours from waste products in carboic acid manufacture by boiling with oxalic and sulphuric acids.
- 1875, July 7th.—Wolff and Betley : Dyes obtained by treatment of naphthaline in which an atom of hydrogen is replaced by one of benzol or its derivatives. No. 2,448.

This notice of the artificial colouring matters may be concluded by a reference to a series of dyestuffs made by the patented process of Croissant and Bretonnière, April 24th, 1873, which consists in heating a variety of organic substances of a neutral nature, such as sawdust, to a high temperature in contact with soda and sulphur; according to the temperature and the materials, a considerable variety of shades of dyestuff can be formed, those produced at the higher temperature being the darkest. The interesting colouring matters thus manufactured have characters more nearly resembling catechu than any other natural body; they are soluble in water, shew a strong affinity for vegetable fibre, dye without mordants, and give very permanent colours to cotton, but unfortunately the shades which can be obtained are all dull and unattractive. For calico printing they present no points of advantage. For dyeing it is possible that the great stability of the colours produced may cause them to be applied for particular

purposes. In 1875 a modification of these dyestuffs was introduced under the name of laval catechu, which is said to be employed by the continental dyers.*

Metallic Colours.—The most important colours which are owing to oxides and salts of metals have been already mentioned. In concluding the subject of colouring matters a few others may be noticed, as well as the attempts which have been made to affix or deposit metals themselves upon fibres, or in other ways to obtain a metallic lustre.

Manganese brown or bronze, was a colour at one time very much in vogue, but disappeared almost entirely about thirty years ago when the dark garancine chocolates came in. This colour was known to Hausmann in the last century, and seems to be indicated in Frith's patent of May 25th, 1798, but the manganese styles were really invented by Mercer many years afterwards. They have been revived to a slight extent in the present year (1877), but are scarcely likely to hold a place in current work. The colour is produced from muriate of manganese fixed by alkali and oxidized in the air, or by dilute bleaching powder. The colour was a dark bronze brown; it admitted of variation by printing discharges of various colours upon it.

The use of fatty soaps of copper for a green colour has been mentioned. It is very old, but was patented

* See Bull. de Mulhouse, xliv., p. 465; Bull. de Rouen, iv., p. 61; Textile Colourist, ii., p. 73.

as new by Humfrey, April 23rd, 1850, and again by Lake, from Wiedershold, August 26th, 1867. The suboxide of copper was fixed by Bancroft; it is a yellow orange shade of but little beauty. Subcarbonate of copper was formerly used as a green dye; the prussiate of copper which Bancroft thought a great discovery has not been found applicable.

Versmann patented, March 25th, 1861, a green colour from prussiate of Titanium, but I believe it has not proved of any practical use.

The action of lead upon wool along with lime or other alkalies to produce dark or brown shades by the action of the sulphur naturally contained in the fibre was patented by Reuter in two patents, dated November 4th, 1862, and December 1st, 1862. Molybdenum, tungsten, and cobalt have also been suggested as sources of colouring matters. The sulphurets of arsenic dissolved in ammonia have been used for yellow colours; the iodide of mercury has also been employed as a scarlet colour. At one time brown colours from sulphuret of antimony were in use for printing and dyeing. Of pigment colours with metallic bases very few have been found to be available for the purposes of the printer beyond those already mentioned. Many natural ochres give agreeable shades, but they are difficult to print, either from persistent sticking in the engraving or from the presence of gritty particles.

The following notes refer to the printing of metals in leaf or in powder and production of metallic

lustres. In Overend's process, patented February 13th, 1844, a composition of linseed oil and gold size is printed, and the metallic powders sifted on. For obtaining a metallic lustre upon woollen goods, Schischkar's patent of November 18th, 1852, consists in preparing the goods with nitro-muriate of tin, afterwards impregnating them with sulphate of copper, and steaming. For the same purpose Depouilly's patent of July 2nd, 1853, is for exposing the goods dipped in metallic solutions (preferably alcoholic or ammoniacal solutions of metals) to vapours of phosphorous or phosphuretted hydrogen. With the same intention Schischkar's and Calvert's patent of January 5th, 1854, is for impregnating goods with salts of lead, copper, or bismuth, and then submitting them to the action of sulphuretted hydrogen gas, or to steam containing sulphuretted hydrogen. Tolson's patent, November 20th, 1855, is to obtain lustre by mordanting in sulphate of copper, and dyeing; then treating again with sulphate of copper and excess of ammonia, washing, and immersing in hyposulphite of soda. For fixing gold or silver leaf or powder upon fabrics, Ruding's patent of December 11th, 1855, claims the preparation of a fine dry powder of shellac obtained by precipitation from alcohol; this powder is dusted over the cloth, the metal leaf or powder being applied by a heated printing surface. For metallic lustres, Schischkar's patent of February 1st, 1856, is for printing or padding with salts of copper or lead mixed with various deoxidizing agents, and

then submitting the goods to the action of high-pressure steam. Taylor's patent for applying metallic powders or leaves, dated December 24th, 1856, consists in an arrangement of the printing machinery by which one roller applies the adhesive varnish and the metal is applied immediately afterwards. The application of steel dust in granulated sparkling powder to textile fabrics in design was patented by Thièbaut. In Forrobert's patent, February 25th, 1860, it is stated that silk boiled with chloride of zinc, washed, and then boiled with finely-divided gold or silver powder, attracts the powders and becomes coated with the metal. For a cement or mordant upon which flock, metal in leaves, or powder, etc., may be deposited, Thièbaut, July 16th, 1860, prescribes 1 quart of soft copal, 1 pint of poppy oil, and 2 oz. of lard, dissolve by heat, cool, and add zinc white and oil according to the nature of the fabric. This size, after printing, is exposed to the air until it is dry enough to be hot pressed. Denham's patent, November 2nd, 1860, refers to a method of applying leaf metal to velvet by heating embossing rollers, and speaks of a compound powder used in the trade, and supposed to be a mixture of rosin and dextrine. Verkrügen's patent for applying gold and silver powders to pile fabrics, dated January 29th, 1861, is by means of sable pencils, and appears more artistic than mechanical. In Diess and Condoreau's patent of April 15th, 1862, which is for applying gold and silver leaf to fabrics, it is directed to prepare a double

stencil plate with a counterpart which will fit into the cut out parts. The gold or silver leaf is introduced between the two cut plates, and placed upon the part of the fabric to be printed; the counterpart is then brought down upon the plates, and forces out the leaf. For depositing silver from solutions upon silk, Cimey's patent of August 18th, 1862, may be consulted. It includes the treating of the silk, in the first place, with the juice of some acid fruit containing tannin, as currants for example; then treating with nitrate of silver and Rochelle salt, and burnishing. Bennet's patent, April 19th, 1875, refers to bronze, brocade, or gold patterns, and proposes to produce the results more economically by printing the adhesive matter with copper or surface roller, and then passing the cloth through a box containing the required metallic powder, which is caused to adhere to the size by means of running the cloth under a roller which works in the metallic powder.

The styles in which effects are obtained by the direct application of metals are at present few, and generally for exportation to semi-civilized communities; but that is because the results are crude and imperfect, and have nothing of the delicacy and finish demanded for garments and furniture required by a more advanced taste. There can be no doubt that any process which could gild or silver fibres in an even and tolerably permanent manner would become of great value. There are processes by which gold and silver leaf can be applied to cover threads in a

fairly satisfactory manner for some purposes ; they are purely mechanical, and only applicable to threads. The methods by which metals can be chemically deposited upon fibres leave nearly everything to be desired. Not included in the patents above, is a process of applying metallic tin by printing and burnishing by calender, which has been applied to some extent upon dyed goods.

RESISTS AND DISCHARGES.

Resists and Reserves.—The application of wax to preserve certain parts of cloth from the entrance of the dye is the first instance we know of the use of resists. This contrivance was found employed by the Hindoos before printing was practised in Europe, and is probably very ancient. Wax is still employed amongst Oriental dyers as a resist in dip-blue dyeing, and in the production of some compound styles from indigo, catechu, and madder.* It is now very rarely employed in Europe, but various fatty compounds are still used alone in silk printing as resists in cold dyeing. The nature of the resist proper to be used to protect the cloth must of course depend upon the nature of the colour or mordant to be resisted, and the way in which they are brought into contact with the cloth. The simplest case of resist is that where a mordant or colour is applied as in calico printing. Here the quantity of mordant or colour to be resisted

* See description of the Batick style of print, *Textile Colourist*, iii., p. 160, from *Moniteur Scientifique*, March, 1877.

is known. Less simple cases are those in which the resist has to preserve the cloth white when dipped in cold dyeing solutions, as for example in indigo dyeing, where the quantity of colour acting upon the resist is not exactly known, and the time during which it has to resist it is relatively considerable; and, lastly, difficult cases where the cloth has to be preserved from the action of hot dyeing solutions for a considerable length of time.

In calico printing the agent chiefly used for resisting mordants is lime juice, the active principle in which is citric acid. In all those cases where a simple acid resist will suffice there is nothing so suitable or so safe as lime juice. When iron, alumina, and other metallic mordants fall upon a lime juice resist of sufficient strength there is formation of a citrate of the metal with some excess of the acid, and the special value of citric acid is that most of its salts are not decomposed by a moderate heat or moisture, that they are soluble, and that metallic oxides combined with it lose almost entirely their mordanting and other distinguishing chemical properties, being overpowered, or as it is said, masked in a remarkable manner by the properties of the acid. No other available acid acts so well as citric acid. Oxalic and tartaric acids form salts with oxides, such as iron, which are soluble at first and would wash off the cloth, but in a short time insoluble subsalts form and fix upon the cloth giving bad whites in dyeing. The same defect is found in the use of such acid salts as

bisulphate of potash, or with such mineral acids as phosphoric acid and arsenic acid, so that practically lime juice (or citric acid) is the only substance that can be used when good whites are required by resisting.

In general the commercial lime juice answers all requirements in a satisfactory manner, but there have been seasons when all lime juice was so poor in citric acid and so overloaded with impurities that no good whites could be got in any class of work, and especially in those cases where a strong colour, such as garancine chocolate, or logwood black, fell upon the acid. In many fine styles of prints a good white is a most important condition, and printers have had to use crystallized citric acid, or to submit the crude lime juice to a method of purification, so as to remove the impurities which prevented the action of the acid contained in it. A method of improving inferior qualities of lime juice consists in following out to a certain extent the process used by the manufacturers of citric acid—first treating it with animal charcoal, precipitating the citric acid as a citrate of lime, washing this and decomposing it by sulphuric acid to obtain a solution of citric acid nearly free from impurities.* The best thickening to be employed with lime juice is calcined farina, probably because when dried it is less easily penetrated than softer thickenings, and the mordant to be resisted is kept to some extent at least at a distance from the fibre. This resist may, however,

* See Textile Colourist, i., p. 5.

be looked upon as a pure chemical resist and almost the only one in use.

Tartaric acid in the form of tartrate of chromium made by acting upon bichromate of potash with tartaric acid, is a useful resist in several cases where citric acid does not answer ; when mixed with citric acid it is more active.

Citric acid or lime juice neutralized with soda is advantageously employed in several cases where the free acid might lead to accidents, as for example, in some steamed styles ; but it is liable to run with moist steam. Tartrate of chromium when used as a resist for steam colours is less inclined to run than citrate of soda, but it leaves a stain upon the cloth not easily taken out without the use of soap, and cannot therefore be well employed in general styles ; it seems well fitted for the steam alizarine styles.

Arsenate of soda and some other neutral salts are capable of acting as resists under mordants and colours, but without the help of pipeclay are not to be depended upon.

Pipeclay is one of the best of the mechanical, inert, resisting agents. It acts simply by covering the fibre with a coating of clay, which when dry, is nearly impermeable to water and dyeing materials. It cannot, however, as before-mentioned, be advantageously used in roller printing for two reasons—first, it is never free from grit, which cuts the doctor and scratches the roller ; and, secondly, it cannot be well put on in sufficient quantity. It is therefore only

used in block printing; its preparation and application requires a good deal of care to secure good results.

Almost the only practical cases of resists used in dyeing are those connected with the indigo styles, which have been previously referred to. It is evident that such a resist must be either at the commencement insoluble in the dyeing fluid or must become so upon dipping in it. Wax and resinous bodies alone fulfil the condition completely; but, as in indigo dyeing, there are many resists which contain matters soluble at the commencement, but they become insoluble on contact with lime or from compounds of very slow solubility. None of these resists can be used for dyeing in warm liquids. For resisting hot dye liquids there is nothing but the purely mechanical means of so covering, pinching, tyeing, or compressing the cloth between solid surfaces that the liquor cannot get to the cloth. This is, of course, very difficult, and not much applied, though many attempts have been made in that direction.

Some of the patented processes referring to resists are interesting, and may be briefly noted. Pottram and Taylor have a patent, dated July, 1781, for producing effects by systematically tyeing up parts of silk handkerchiefs so as to preserve those parts from the dye. Quite recently I have seen large rugs for the African market dyed up with this kind of reserve. The effects were, of course, irregular, but not unpleasing, and when dyed a second time in another colour, either with or without freshly tyeing up,

very curious results were produced. Nathaniel Watts' patent, November 22nd, 1787, is for producing designs upon small pieces of cloth, such as waistcoats, by dyeing. The cloth is tightly compressed between two metal plates, on one of which the pattern is cut out, and the other has small holes to admit the dyeing liquor. When thus secured they were plunged into the boiling dye bath. Similar is Bailey's patent, November 28th, 1792, for producing patterns in dyeing by nipped reserves. Blocks were fixed in frames, the handkerchiefs to be dyed put between two frames, and fastened; the blocks pressed the cloth tightly, so that the dye did not gain access, and the parts remained white. The plan of resisting by means of waxy, fatty, or resinous bodies was the subject of a patent to Duffy, February 8th, 1814. A curious attempt to compose a resist which would withstand the action of boiling liquids is recorded in the patent to Richardson and Hirst, July 26th, 1825; it was for application upon woollens, and was to be made from 5 stones of flour beaten up in 4 gallons of water, which, after standing two or three days, was mixed with the whites and yolks of forty eggs. After having performed its function it was to be removed by soaping. A mechanical reserve in roller printing was patented by Dalglish, December 6th, 1830. It was intended for reserving in white a cross bar while printing a cover or padding, and was effected by having two belts or cross straps attached at fixed distances, upon which the colour fell instead

of upon the cloth. The patent of Robinson, June 27th, 1857, is for reserving, saving, or stopping in dyeing by means of blocks of wood screwed tightly together with the cloth between. Another patent of November 3rd, 1845, is very similar, with some supposed improvements in processes for securing the blocks. Christen's patent, September 19th, 1850, is for reserving whites in roller printing by interposing an endless fabric composed of several thicknesses of calico cemented together by gutta-percha between the roller and the cloth to be printed, parts of this fabric being cut out in proper patterns. For reserving in dyeing, Warmont's patent of November 2nd, 1850, resembles some of the older ones where the cloth is compressed between two surfaces and the dye liquor so kept out. Sulphate of manganese is proposed by Leese, January 26th, 1855, as a resist in indigo blue dipping. Means of reserving in piece dyeing by means of pressing surfaces are again patented by Hargreaves, March 25th, 1856. Reserving or "saving" the lists of textile fabrics so that they shall not receive colour in the dye is referred to in Riley's patent, October 3rd, 1857; this, it is said, was formerly done by hand sewing of a web or binding over the edge or list of the fabric, in this patent the list is rolled and sewed by a sewing machine. A method of using gum as a resist for an alcoholic tincture of alkanet is given in Lewis' patent of April 1st, 1861. The cloth to be dyed is first prepared with alum and then printed in a design with

gum water, dried, and passed through methylated spirit, and afterwards in the solution of alkanet, steamed and washed; the gum being coagulated by the alcohol, acts as a resist, and preserves the printed parts white. Reserving plush fabrics by means of stencil plates and colouring by brushing the colour through the openings is patented by Dickins and Heywood, February 23rd, 1863. Miller and Laing's patent, May 28th, 1865, refers to the means of interposing thin sheets or plates of zinc of given forms between the roller and cloth while the printing machine is running, so as to reserve white parts which can afterwards be printed with other colours. They state that formerly paper was used for this purpose, and they do not claim the principle, but only certain accessory guides which keep the metal sheet in its proper place while passing under successive rollers. A resist for aniline colours patented by Durand, December 19th, 1865, consists in printing zinc dust mixed with bisulphite of soda or with acid bodies which do not act upon zinc at ordinary temperatures, such as arsenious acid or bisulphate of potash; these compositions can also be used as discharges. For reserving or saving lists of dyed woollens, Hinchcliffe's patent of January 24th, 1866, describes machinery by which a cord is stitched and covered on the list so as to prevent the entrance of the dye. The use of gum resins, caoutchouc, shellac, etc., as resists to withstand dyeing, is claimed in Greenhalgh's patent of February 17th, 1866. After dyeing,

the resists to be removed by suitable solvents, as alcohol, ether, naphtha, etc. Pilling and Jennings, in their patent of August 13th, 1867, describe a method of reserving the edges of woollen fabrics by securing a closely-woven web stitched on them. In Gatty's patent of February 21st, 1872, a kind of resist, or, as he says, a waterproof colour, is made by adding lime, soap, resinous bodies, or tallow to ordinary colours, which will then not absorb another colour printed over them. Whiston, September 24th, 1873, patents the use of hot wax as a resist for aniline colours which are to be dyed cold, and afterwards removing the wax by benzine or other solvents.

Anything which covers the fibre will act as a mechanical resist so long as it can retain its place on the fibre, but nothing has yet been found which satisfactorily fulfils this condition in warm dyeing combined with motion of the goods. Gum water alone has been profitably used in some steam styles as an imperfect resist, or perhaps more properly, a dilutant of colours falling upon it, so that from an eight-coloured pattern, one of the rollers being engraved to print gum water so that it should fall partly under the colours of a number of the other rollers, double shades could be produced, and the effect of twelve or fourteen colours more or less imperfectly obtained.

The above cases of resisting have the simple object of preserving the white or natural colour of the cloth. There are other cases which have been worked out by

the ingenuity of printers where the resisting body is combined with a colouring matter or a basis upon which a colour can be dyed. Instances of the former class are rare, and seldom employed in printing; resist catechu brown is an illustration. Examples of the latter class are more numerous, as in the orange resist for indigo styles, the red mordant resist in the neutral style, or the red mordant with tin salts, which resists iron mordants, and some other cases of less importance peculiar and limited to special colours and combinations.

Discharging.—Discharging is the destruction and removal of mordants or colouring matters already existing on the cloth, the general intention being to obtain a white object upon a coloured ground. This method of procedure for procuring designs or patterns appears to be of much more modern date in calico printing than that of resisting. It requires active chemical agencies. The first account that I find of the use of acids in discharging is contained in a patent to Gillespie, April 30th, 1799. He mentions that acids had been previously used for resisting, but claims their use in discharging as his discovery. The other agents chiefly used for discharging colours, as bleaching powder and bichromate of potash, only came into the hands of printers within the present century. The discharging of mordants to be afterwards dyed is not much practised except in the logwood black styles. Sharper and clearer impressions of white can be got by discharging than by

resisting, because in resisting the acid always spreads a little, producing a white larger than the impression. Allowance cannot always be accurately made for this in the engraving; but, on the other hand, the whites are generally purer by resisting than by discharging, for it is difficult to remove all traces of mordant. Lime juice or citric alone is too feeble for discharging, and is generally used in combination with oxalic and tartaric acids, and sometimes with other acid bodies, as bisulphate of potash.

The chief cases of discharging dyed colours are in connection with indigo (which have been treated of), and Turkey red. The use of bleaching powder for producing white objects upon a Turkey red ground by first printing an acid upon it and dipping in solution of bleaching powder was discovered by M. D. Koechlin, and applied by him in 1811, and afterwards further developed by Thomson; the use of chlorine solutions applied directly to the cloth, compressed between perforated leaden plates, appears to have been the discovery of Monteith, who worked it largely about 1820, for the so-called Bandana style. The method of obtaining a yellow discharge by adding lead salts to the acid in the first process and afterwards chroming has been largely applied, not only to Turkey reds, but also to common madder reds and pinks, and to some extent also upon madder purples. Prussian blue is discharged by means of caustic alkali; iron buff, manganese brown, and some other mineral colours are discharged by acid muriate of tin. Many ingenious

devices for discharging a given colour and replacing it by another one have been practised in the past, but very few of them were largely applied, and scarcely any are now in use.

Of patented processes referring to discharging which have not been previously mentioned, the following may be noted :—Improvements in the discharging press for Turkey reds, patented by Muir, August 26th, 1839; a vacuum is caused by condensation of steam, and the liquor drawn through the cloth. Kopp and Gatty, December 9th, 1852, patented the use of arsenic and phosphoric acids at a strength of 170° Tw., as substitutes for tartaric acid. Graham's patent, of April 13th, 1861, is for producing a black upon Turkey red cloths in conjunction with the discharging press. After the mixture of sulphuric acid and chloride of lime has been passed through and discharged the colour, it is followed, in those places which are to be made black, by acetate of lead and bichromate of potash; the chromate of lead thus formed acts as the basis or mordant for the black, which is produced by the subsequent passage of logwood liquor at $2\frac{1}{2}^{\circ}$ to 4° Tw. A less good black is said to be produced by iron salts with logwood. For discharging aniline colours there are patents to Keymer and Whitehead, March 15th, 1867, and to Whitehead, September 13th, 1867, in which an alkali is printed on the colours, and the goods are steamed in a box which contains red prussiate of potash with oxalic acid; it is said the hydrocyanic vapours destroy the colours where the alkali has been printed.

GENERAL FINISHING PROCESSES.

Clearing of Whites.—The old method of clearing whites after dyeing consisted in extending the pieces on grass, where the action of air, light, and moisture gradually destroyed the small amount of colouring matter which remained on the unprinted parts of the cloth. The printed colours themselves were but slightly affected, and in some cases distinctly improved by grassing, notably madder reds and pinks. The time of exposure required to bleach the whites, other conditions being equal, varied according to the amount of solar light. In summer and in bright sunny weather, one or two days sufficed; at other times the progress might be very slow, occupying from several days to several weeks in the winter season. Soon after the introduction of chlorine into bleaching it was shewn that bleaching powder could be used for clearing whites of dyed goods, and it was put into use in the seasons unsuitable for grass bleaching at the early part of this century, but did not become general for a considerable time afterwards on account of the care required in its application, and the numerous accidents to colours which happened from its use by unskilful workmen. The many inconveniences attending grass clearing, the growing cost of labour, and a better knowledge of the powers of bleaching powder led at length to a general adoption of clearing in the dyehouse, and the almost universal abandonment of crofting, at least in England,

though in other countries it was carried on to a recent period, and may even yet be seen in operation in parts of the continent where labour is not so costly nor time so precious to the manufacturer.

Clearing in the Beck.—Up to about 1848 the usual method of clearing all dyed work was in a beck similar to the dyebeck, the pieces being entered, the water heated or in some cases cold, and as much solution of bleaching powder added as the experience of the clearer had shewn to be required. It was a very uncertain process, and required a skilful operative to look after it, who, judging by the appearance of the goods, and seeing how much the colour would stand, adapted his strengths, temperatures, and times to the varying conditions under which he had to work, it being impossible to lay down any fixed rules as to time or proportion of material. The method, however, was fairly satisfactory as far as regarded soaped work—that is, madder work—the colours being fast and the previous soaping appearing to protect the colours from the action of the chlorine. When styles of dyed work came into vogue which did not require or would not stand soaping a difficulty was found, and especially with the dark garancine styles, the whites could not be made pure and bright without great risk of injuring the colours. This state of affairs stimulated enquiry into other means of clearing, and led to the invention and adoption of the modern system of clearing by machine.

Clearing by Machine.—It would appear that the

system of clearing by application of relatively strong solution of bleaching powder by means of engraved rollers originated with the house of Bleck, Steinbach, and Muntz, in the winter of 1846-1847. Priority has been allowed to this firm for the discovery by the Chemical Section of the Mulhouse Society, though it is admitted that at Schwartz-Hugenin's and other houses a similar or identical process was in use at very nearly the same date.* Messrs. Royet and Steinbach report that after many trials of the best way of effecting the object in view, they adopted, in the spring of 1847, the method of applying the bleaching powder solution by means of a fine pin roller, and immediately passing the goods over steam chests, and this in preference to the plan, now found most efficient, of steaming directly after the application of the bleaching solution, and before drying.

The many modifications of this system of clearing have been very generally abandoned in favour of the method of applying the bleaching or clearing solution by means of an india-rubber coated roller, the cloth passing between this and a plain brass or copper roller, and then immediately into a steaming box. The cloth may pass through the trough containing the bleaching liquor, and then between the two rollers, or it may obtain its supply of the liquor from the india-rubber roller revolving in it, and without passing

* See Memoir and Report upon this subject, Bull. de Mulhouse, xxvii. (132), p. 232. The process was not patented. In Johnson's patent, October 17th, 1850, clearing by padding in chemic and drying over tins is claimed.

through the liquor, the former method being, I believe, preferable.

A complete chloring arrangement, as at present fitted up, consists of the padding machine; a steam box close to it; a washing arrangement, which may be combined with a water mangle, which straightens, smooths, and squeezes the cloth; and a drying machine.

The working of this arrangement requires but little description. The strength of bleaching solution for the particular style is found by a few trials; the steaming box should be well supplied with steam, so that the cloth may be heated to 212° , and almost instantly, in such a box, fifteen to thirty seconds of time is amply sufficient. The cloth should not taste of bleaching powder after it has passed through the steaming box, and then a very slight washing is sufficient to remove the soluble matters remaining on it.

This system of clearing is applicable to all kinds of work, for the strength of bleaching liquor can be nicely apportioned so as not to injure the most delicate colours, and it is now usual to send all work through the chloring arrangement to perfect the whites, as well as to smooth the cloth, which greatly facilitates the evenness of the starching. But a single passage is not sufficient for all styles, as for example, dark and heavy garancines; in some establishments such styles are first cleared wet, that is, direct from the squeezers, and a second time dry.

There have been some suggestions as to the use of other substances along with bleaching powder for

clearing which may be briefly noticed. To avoid injury from the decomposition of the chloride of lime in the beck process by acid waters, or waters containing much carbonic acid or bicarbonates, it is useful to add a little carbonate of soda; the clearing powder which was used by some houses was a mixture of crystals of soda and common bleaching powder. The use of acids in clearing was formerly practised; crabs and lemons are spoken of in old books; sour brewers' grains are claimed in Grimshaw's patent, February 17th, 1796; this was before chlorine was employed. Hughes, in his patent of July 13th, 1855, claims as a great improvement adding silicic acid to solution of bleaching powder. Sacc states that zinc salts added to bleaching powder gave it great energy. Henri A. Koechlin proposed to clear prints by padding first in bleaching powder by a pin roller, and immediately afterwards applying dilute muriatic, acetic, or sulphuric acid by another pin roller. Fleming's patent, August 20th, 1863, is for clearing and starching in combination. In some cases bleaching liquor has been added to the starch to correct bad whites; pieces which have been starched may have bad whites improved by the chloring process, but it will be found that the conditions are different; the starch takes up a good deal of the liquor, and it must be used weaker than for unstarched goods.

Starching.—The greater bulk of printed and dyed cotton goods undergo some sort of stiffening operations before going to market, the object being to make

them look new and fresh. It may be said that all colours are, more or less, injured in beauty by the addition of finishing materials, hence such colours as Turkey reds or Indigo blues in certain styles, where the display of the design is of inferior importance to the appearance of a rich saturated colour, are frequently delivered with no further finishing than smoothing out and folding. Other styles of prints are highly stiffened and mangled, or even receive a high polish by means of calendering. The ordinary class of prints for home consumption in England are but lightly starched, and smoothed by passing between a brass and a hard wood roller.

Until recently the method of starching consisted in simply passing the goods through the boiled starch, and expressing the excess by means of rollers, the starch in this case penetrated the cloth through and through in an uniform manner. It was well enough known that the layer of starch which covered the colour, being more or less opaque, was injurious to it, but it was looked upon for a long time as an unavoidable defect. The method of using the starching mangle, by which the piece was not wholly submerged in the starch but received it upon the back from a roller revolving in the starch box was scarcely to be considered any improvement, since it was immediately pressed into the cloth by passing between heavy rollers and would only answer for a light finish. On October 8th, 1860, Underwood applied for a patent for applying the finishing material to the back of the

print by means of a roller, as in the printing machine. This is the first record I find of the idea of back starching, but I believe this method of performing it was not new at that date, and that it had in fact been used for exceptional cases long years before, but it was evidently unsuited for regular use.

Jones' Back Starching Machine.—This apparatus was patented January 1st, 1863, and found to answer the purpose so well that it has been very generally used by the trade with but small changes up to the present time. Instead of passing the cloth to be finished between rollers, whether plain, or plain and engraved, the cloth is passed over an engraved roller which dips in the starch, it is cleaned by a doctor, and revolves in a direction opposite to the motion of the fabric. The roller, as it is described in the patent, is engraved in pinned diagonal lines, which do not run in the same direction, but starting from the centre of the roller go in opposite directions. This was to prevent the narrowing of the cloth, and is even said to increase its width. This, however, is not of much consequence, the rollers now being preferably engraved with a coarse pin. The real merit of the invention was in driving the starching roller in a contrary direction to that of the piece passing over and touching it. In the patent the starching roller is directed to be driven at about the same speed as the cloth, but the actual machine is provided with fittings by which the speed can be changed. The effect is that the cloth rubbing over the roller wipes

out the starch contained in the pins, and if the cloth be not pressed too strongly against the roller, and the starch is of the right consistency, it is nearly all retained upon the one side of the cloth, which is of course the back, very little penetrating to the face. Hence a certain degree of stiffness and finish can be obtained without masking the colours by a comparatively thick layer of the finishing material being placed over them, as in the old system of starching. In order to obtain the full effect of this new method the goods must be dried quickly, which is accomplished by a drying machine placed in connection and arranged to work with steam at a pressure of 10 or 15 lb. per inch; as only the face or unstarched side of the piece can be allowed to come into contact with the heated tins until the starch is partly dried, the drying machine must be either a large cylinder, or, as is most usual, one with the ordinary size of cylinders provided with four or five skeleton or lagged rollers, against which the starched side of the piece alone touches until the starch is sufficiently dried to adhere strongly to the cloth.

Chambers patented, November 20th, 1866, an apparatus which seems to be a modification of Jones'. The starch is supplied to the cloth by a roller revolving in a starch box, an upper roller guides the cloth, and is adjustable, so that the starch need not be pressed into or through the cloth; a doctor is so placed as to remove the excess of starch from the cloth. Pressing rollers may be used to force the starch into the cloth if that is desired. In Livesey's patent of April 2nd,

1870, the cloth goes down into the starch with a bowl or roller, the excess is scraped off with a doctor, and then the cloth passes against revolving brushes and over drying plates. This patent is for starching on one side only, the bowl preventing access of starch to that side in contact with it.

The materials used for finishing prints vary to some extent according to the kind of finish required by the particular market for which they are intended. Potato starch is of very general use as the main ingredient, but other kinds of starches, such as sago, rice, and wheaten starch, are also employed; glycerine, soap, and tallow, or other fatty matter, is commonly added to give softness; china clay and other mineral substances are sometimes used in back starching to give weight, as well as to communicate certain desired qualities of fulness of feel, etc. Scarcely anything is more difficult in all the range of calico printing, at certain times, than to give satisfaction in the finish, and it requires no small amount of aptitude in that branch to please the varying and often divergent tastes of customers. There is no general or admitted standard of excellence of finish, and hardly any useful information can be given as to the principles, being so much a matter of practical knowledge, and results depending so greatly upon small details, as for example in the amount of boiling to which the starchy matter should be subjected, or the quickness or slowness of the drying afterwards, and a multitude of other points.

The boiling of the starch is generally effected in double-cased pans of the same construction as the ordinary colour-shop pans. Arrangements have been made for boiling the starch in closed pans, and under pressure. The more completely a starch is boiled the more gummy and less pasty it is, and it gives a distinctly different finish; a starch but slightly boiled, or thickened without boiling, gives a soft, full finish; when completely boiled, it gives a thin and hard finish. The great quantity of starch paste consumed in finishing has stimulated inventors to produce apparatus by which a continuous supply is furnished. Tunstill's patent of August 19th, 1867, is for pumping the mixture of starch and water into a tube which contains another admitting high-pressure steam through perforations in it. In Hall's patent of December 17th, 1866, the cold mixture of starch and water is pumped up from a cistern into a copper pipe, which is surrounded by another serving as a steam jacket. Steam of any temperature or pressure is admitted, and the starch is boiled and passes along in a continuous manner to the machine where it is used.

Mangling and Calendering.—After starching and drying, the only other treatment for the great bulk of English prints is a simple smoothing and pressing by passing them between bowls of hard wood, such as sycamore or maple, and a brass bowl. This is what is called mangling. It is done with as great a pressure as possible, and afterwards the goods only

require folding and making up. For many markets there is a demand for the calender finish, or as it is sometimes called, the Swiss finish. This is only another kind of mangling, but with greater pressure and differently constructed bowls. The ordinary Swissing calender has three bowls; two of large diameter are made of compressed paper, and the third is of polished iron. The paper bowls are very hard and more elastic than wood, so that they press the cloth more perfectly and more strongly against the iron than a wooden bowl could, and a smooth glossy appearance is communicated to the cloth. To obtain a still higher gloss upon the cloth, what is called the friction calender is employed. This calender is so geared that the metal roller is driven at a slightly greater speed than the paper bowls, and it travels faster than the cloth, rubbing against it with friction, and communicating to it a smooth polish or glaze.

Calendering may be effected either hot or cold. For hot calendering the metal bowl is hollow, and heated either by steam, bars of hot iron, or gas jets.

A necessary operation connected with calendering is damping or degging, the object of which is to soften the starch in the cloth, so that the bowls can act more powerfully upon it. The usual degging machine consists of a box with a revolving circular brush, which dips in a trough of water and sprinkles the cloth passing rapidly before it.

The other operations of finishing, which are but

rarely applied to printed cloth, such as beetling, embossing, stentering, etc., scarcely call for detailed notice here. Some references concerning them will be found in the Appendix.

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NOTE.—The references in the following pages are to serials in which articles bearing upon the subject of this work only appear occasionally, and in which they are buried, as it were, in a mass of other matter. This collection, which could be very greatly extended from the Author's notes, has no pretensions to be complete or exhaustive even for the journals quoted ; it is no more than a selection of those matters deemed the most interesting and important contained in serials extending over nearly a century. For greater convenience, many of the references given in foot notes in the body of the work have been repeated, but none of the numerous patents previously mentioned will be found, except in the few instances where they have been noticed in contemporary publications.

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- Manganese**. Haussman used for brown. *Nicholson's Journ.*, xii., 206, from *Ann. de Ch.*, liii. 208
- Mangling**, Robertson and Orchar's patent for finishing by, No. 2647, Oct. 13th, 1865
- „ Robertson and Orchar's patent for finishing by, No. 1088, April 12th, 1867
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- „ „ Benner on the same. *Bull. de Rouen* iv., 256
- Mercurialis Perennis**, red colour from. *Ann. de Ch.*, vi., 25
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- „ Townsend's patent for use of calcium and magnesium chlorides to prevent, No. 2198, August 5th, 1862
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- „ „ 1861, June 17th, No. 1547, Mellodew and others: This patent refers to velvets and velveteens, and describes several contrivances used to obtain an equal colour on the mixed fibres; mordanting the cotton before weaving, padding the mordant on the back of the piece, etc. See also patents to the same parties, December 6th, 1860, No. 2993, and December 7th, 1861, No. 3075
- „ „ 1862, June 30th, No. 1913, Parker: It is stated mixtures of wool and cotton can be dyed of a uniform shade by well sulphuring

- the goods, and then either dyeing directly or washing out the sulphurous acid and dyeing
- Mixed Fabrics.** 1863, August 1st, No. 1902, Brooman, from Grison: The point appears to be in mordanting at one operation, commencing with an acid mordant, and then at a certain stage of the mordanting adding alkalies to make the mordant neutral; the wool is supposed to take the mordant from the acid liquid, and the cotton afterwards to take it from the neutralized liquid
- ” ” 1864, February 29th, No. 496, Worrall: In union silk-faced velvets dyed black he applies colour to the back of the piece
- ” ” 1864, February 29th, No. 495, Worrall and Cooper: Preparing velvets before dyeing with stannate of soda and alumina
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- ” ” 1864, March 9th, No. 584, Worrall: Refers to union velvets (silk and cotton), which are to be prepared with stannic acid and tannin for dyeing in aniline colours
- ” ” 1864, March 9th, No. 583, Worrall: In union velvets dyeing the cotton a fast colour before weaving
- ” ” 1866, February 3rd, No. 345, Baker: For mordanting before weaving, chiefly for black dyeing of laces and nets. The mordant employed is nitrate of iron
- ” ” 1868, November 20th, No. 3534, Descat and Guillaume: For treating mixed tissues of vegetable and animal fibres by solutions of iron, copper, manganese, and chromium, and passing in an alkaline or chrome bath
- ” ” 1874, January 13th, No. 179, Bird: For

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- Ratanhia**, a Peruvian root yielding colours like catechu. *Roth. Bull. de Mulh.*, xxxv., 212
- Red Clover Seed** used in dyeing. *Ann. de Ch.*, iii., 294
- „ **Turbans**, Indian manufacture of. *Technol.*, viii., 245, 291
- „ **Mordant**, Lennsen on lead in. *Technol.*, xxiii., 574
- „ „ Dullo on preparation of. *Chem. News*, xiii., 108
- „ „ Graham on dialyses of. *Chem. Soc. Journ.*, xv., 249
- „ „ Koechlin upon, *Bull. de Mulh.*, i., 227, 322
- „ **Colour**, Hoffmann's process of making, by acting upon aniline with bichloride of carbon. *Bull. de Mulh.*, xxxii., 503 ; *Comptes Rendus*, xlvi., 452
- „ **Prussiate**, Leeshing on testing of. *Chem. Gaz.*, xi., 139
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- Rhamnine Extract** for dyeing. *Technol.*, viii., 400
- Rhubarb**, red colour from. Garot. *Chem. Gaz.*, viii., 99, from *Journ. de Pharm. et Ch.*, January, 1850
- Rocella Tinctoria**, Schunck upon. *Ann. der Ch. u. Ph.*, lxi., 64
- Rochelle Salt** as substitute for tartar. *Chem. Gaz.*, iv., 125
- Room Dye**, a product from Assam, apparently an astringent substance. *Journ. Soc. of Arts*, ii., 818
- Rosolic Acid**, account of labours of Runge, Hugo Muller, Angus Smith, and Jourdain upon. *Technol.*, xxii., 585 ; *Chem. Gaz.*, xvi., 20

- Rosolic Acid**, Kolbe's description of preparation. Technol., xxiii., 359
- „ „ Fresenius upon. Mon. Scient., xiv., 371, 373.
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- Rubian** and its decomposition products. Chem. Gaz., ix., 117;
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- Safflower**, Schlieper's examination of. Chem. Gaz., iv., 376,
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- „ or carthanine. Ann. de Ch., xxviii., 312; xxx., 156;
xlvi., 312; l., 73
- Saffranine** made from nitrate of aniline and arsenic acid. Technol., xxxii., 62; Must. Zeit., 1870, No. 25;
Hoffmann's analysis, Mon. Scient., xv., 237
- Santal Wood**, Weidel and others upon colouring matters in.
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- „ Meier upon. Chem. Gaz., vii., 130, from Archiv. de Pharm., iv., 285; lvi., 41
- „ Weyermann and Haeffly upon. Chem. Gaz., 353, from Liebig's Ann., 1850, p. 226
- „ method of dyeing with. Chem. Gaz., x., 235
- Sarassin paille de**, colouring matter of. Technol., xi., 472
- Scarlet** upon cotton, new process. Ann. de Ch., l., 147
- Schlossberger's** solvent for silk. Chem. Gaz., xvi., 372
- Sepia Colour**, by action of sulphuric acid on sugar. Chem. Gaz., i., 666
- Serum of Blood** used in Turkey red dyeing. Ann. de Ch., iv., 119
- Silica**, Reimann on action as a mordant. Technol. xxxii., 13, 118;
Chem. Centralbl., 1871, p. 61; Chem. Soc. Journ., xxiv., 452; Chem. News, xxii., 83
- Sheep Dung**, use in Turkey red dyeing. Ann. de Ch., iv., 143;
xxi., 196
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- „ Mené's numerous analyses of raw. Technol. xxxi., 134

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- „ Spiller on solution of, in hydrochloric acid. *Chem. News*, xxii, 169
- „ method of degumming or boiling off. *Technol.* xxx, 84
- „ Persoz on weighting of, and liability of weighted to fire. *Technol.*, xxx, 295, from *Comptes Rendus*, lxxxvii, 1219
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- „ black example of spontaneous combustion of. *Chem. News*, xxii, 144, from *Dingler's Journ.*, July, 1870
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- „ Grüne upon gilding and silvering. *Chem. Soc. Journ.*, xxiv, 450, from *Chem. Centralbl.*, 1871, p. 174
- „ Mulder's analyses of. *Bull. de Mulh.*, xi, 164
- Silk Bleaching**. Nicholson's *Journ.*, i, 32, 88, from *Journ. de Phys.*, xlii, 376; *Ann. de Ch.*, xlvi, 206; liii, 249
- „ **Dyeing**, Indian methods of. *Technol.*, viii, 17, 54, 102
- „ „ Johnson's patent for weighting by sub-acetate of lead, March 14th, 1853
- „ „ Oldham's patent for dyeing waste, No. 3117, Nov. 20th, 1862
- „ „ Müller's patent for treating with acids and salts, No. 1294, May 3rd, 1867
- „ „ Dickens and Heywood's patent for washing and dyeing, No. 3618, Nov. 27th, 1868
- Singeing**, Schultz on comparison of various methods. *Bull. de Mullh.*, xxxvii, 533
- „ Tulpin's machine figured in *Must. Zeit.*, 1868, No. 1
- Smoke**, Streat's patent for dyeing or staining by, No. 121, Jan. 17th, 1867
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- „ Bolley on valuation of. *Chem. Gaz.* xi, 55
- „ Hughes, patent to, for treating soap liquors, No. 913, March 13th, 1874

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- Soap Worts**, Bleckrode on ancient use of in bleaching, and present use in the Levant, etc. *Journ. Soc. of Arts*, viii., 105
- Soga, Zoga, or Coua**, an astringent bark examined by Bolley. *Technol.*, xxvii., 26
- Sorgho**, Clouet upon a farinaceous matter called Dari, or, *Bull. de Rouen*, iv., 379
- Stannates**, Greenwood, Mercer, and Barnes' patent for making dry stannate, July 8th, 1845. *Chem. Gaz.*, iv., 127
- „ Mercer and Blythe's patent arseniate-stannate. Oct. 12th, 1849. *Chem. Gaz.*, viii., 367
- „ Higgins' patent alumino-stannate, Nov. 24th, 1862. *Chem. Gaz.*, xi., 440
- Starch**, Chevreul on obstinate adhesion of, to cotton. *Chem. News*, v., 42, from *Comptes Rendus*, liii., 984
- „ use with mordants for dyeing. *Ann. de Ch.*, iv., 116, 144
- „ existence of, in flax. *Ann. de Ch. et Ph.* (3), xviii., 168
- Steaming** printed goods, observations upon. *Bull. de Mulh.*, vii., 195; *Technol.* i., 351
- „ Richards upon a new system of. *Bull. de Rouen*, ii., 93; Reber's report upon this communication. *Bull. de Rouen*, ii., 95
- Straining**. Glanzmann's modification of Rosenstiehl's apparatus. *Bull. de Rouen*, iii., 121
- Stentering**. The following patents refer to finishing by stentering frames to produce what is usually called the elastic finish :—
- „ Norton: Heating the cloth on both sides, No. 2386, Oct. 2nd, 1860
- „ Brown: Shortening the machine, No. 2896, Nov. 7th, 1866
- „ Cochran: Improvements in clamping, No. 3612, Dec. 19th, 1867
- „ Lowndes: Clamps instead of pins, No. 1174, April 7th, 1868
- „ Whiteley: Stretching and finishing, No. 1648, May 20th, 1868

- Stentering.** Henderson: Details in the clamps, No. 1910, June 11th, 1868
- „ Cochran: Clamping bars, No. 1976, June 18th, 1868
- „ Lowndes and McCallum: Clamps, No. 226, Jan. 25th, 1869
- „ Knowles and Green: Driving, No. 347, Feb. 4th, 1869
- „ Henderson: Holding selvages, No. 1410, May 8th, 1869
- Stretching.** The following patents refer to stretching and widening cloth:—
- „ Bush: Widening while drying, June 14th, 1834
- „ Worrall and Race: Stretching and drying, No. 497, March 12th, 1858
- „ Hesford: Stretching, No. 1122, May 20th, 1858
- „ Clark: Stretching and drying, No. 394, Feb. 13th, 1860
- „ Harwood: Stretching and drying, No. 3051, Dec. 12th, 1860
- „ Senior: Stretching woollen goods, No. 70, Jan. 11th, 1861
- „ Lunn and others: Widening and stretching, No. 1046, April 26th, 1861
- „ Renshaw and Howorth: Stretching, No. 2333, Sep. 22nd, 1863
- „ Wydler: Steaming during stretching, No. 1861, July 26, 1864
- „ Norton: Stretching woollens, No. 2685, Oct. 29th, 1864
- „ Hosford: Stretching after bleaching, No. 1317, May 12th, 1865
- „ Worrall and Hughes: Stretching, No. 1360, May 16th, 1865
- „ Stead: Opening and extending, No. 833, March 21st, 1866
- „ Hetherington: Widening, No. 1640, May 29th, 1868
- „ Birch: Opening and spreading, No. 4234, Dec. 24th, 1873

- Stretching.** Heilmann's machine. Bull. de Mulh., xxxviii., 375
 „ Dennison's machine. Must. Zeit., 1866, p. 1
- Sublimate Corrosive**, action in madder dyeing. Ann. de Ch.,
 iv., 148
- Sulphates**, influence in madder dyeing. Ann. de Ch., iv., 132, 147
- Sulphate of Indigo**, uses in dyeing. Chem. Gaz., xii., 79 ;
 Ann. de Ch., lviii., 189
- Sulphuric Acid**, action in bleaching and upon indigo. Ann. de
 Ch., xi., 187
 „ action of upon colours. Ann. de Ch., xv., 101
- Sulphurous Acid**, action of upon colours. Chem. Gaz., x., 15 ;
 Ann. de Ch., xi., 63
- Sugar** as solvent for indigo. Ann. de Ch., xxii., 100
 „ effects of in madder dyeing. Ann. de Ch., iv., 144
- Sulphur**, Lauth upon, as a mordant. Mon. Scient., xv., 796 ;
 Bull. de Mulh., xlv., 422
- Sumach**, analysis of remarks upon. Technol., xii., 305 ; xv., 156
- Syria**, an animal matter used in dyeing. Technol., i., 348
- Tannin**, substitute for in extract of bark of hemlock tree. Nor-
 ton's patent, No. 3633, Nov. 28th, 1868
 „ substitutes obtained by treating spent tanners' bark, etc.
 Mucklow's patent, No. 2042, June 25th, 1868
 „ artificial, by action of nitric acid upon bituminous bodies.
 Ann. de Ch., lvii., 116
- Tannic Acid**, Calvert upon. Chem. Gaz., xii., 440
- Tar Water**, dyeing with. Chem. News, xviii., 200
- Tartaric Acid**, Murdich's substitute, salt, nitric acid, etc. Chem.
 Gaz., iv., 48
 „ „ Benckiser recommends Rochelle salt as preferable
 to tartar in dyeing. Chem. Gaz., iv., 125, from
 Archiv. der Pharm., xliii., 144
 „ „ Carteron's patent for substitute, Feb. 5th, 1849.
 Chem. Gaz., vii., 368
 „ „ Bolley recommends phosphoric acid as substitute.
 „ „ Kuhlmann proposes tartrate of baryta for dyeing.
 Technol., xxiii., 237
 „ „ Roth upon adulteration of tartar. Bull. de Mulh.,
 xxxvi., 481
 „ „ Oliver's patent for substitutes, Nov. 11th, 1849

- Tartaric Acid**, Kopp and Gatty's patent for using arsenic and lactic acid as substitutes, Dec. 14th, 1853. Chem. Gaz., xii., 452
- „ „ Johnson's patent for substitute, chiefly sulphate of alumina, Dec. 16th, 1853
- „ „ Barcroft's patent for arsenic acid and salammoniac as substitutes, April 30th, 1857
- Tartrate of Alumina** as mordant. Ann. de Ch., vii., 240
- Tartrates, Alkaline**, influence of in dyeing. Ann. de Ch., iv., 146; v., 105
- Thuja Occidentalis**, tannin and colouring matters in. Chem. Gaz., xvii., 88
- Tentering**, Kempe's patent for tentering and drying, No. 883, April 3rd, 1871
- „ Broadbent's patent, No. 3,752, Oct. 30th, 1874
- Thao**, Heilmann and Reber upon uses of as a thickener, etc. Bull. de Rouen, iv., 258, 261
- Tin**. Muller and Kopp state they can deposit 25 per cent. of oxide of tin upon calico by means of permanganate. Technol., xxxiii., 59, from Chem. Centralbl., 1871, No. 37
- „ fixing of upon cotton. Ann. de Ch., xii., 216
- „ solutions of, uses, and peculiarities in dyeing. Ann. de Ch., ix., 152
- „ salts, preparation for dyeing and printing. Technol. i., 301; xi., 411
- „ salts and quercitron bark. Ann. de Ch., xxii., 100
- Tin Oxide**. Lowenstein on precipitation of peroxide of tin by alkaline sulphates. Chem. Gaz., x., 338, from Journ. für Prakt. Ch., lvi., 366
- Tungsten**, colours from, Emmerson's patent. Chem. News, i., 189
- „ and glue as albumen substitute. Sonnenschein, Chem. News, xxii., 215, from Dingler's Journ., Sept., 1870
- Turkey Red**, Maclachan on the method in use by the natives of the Coromandel coast for producing. Nicholson's Journ., ii., 296; Trans. Soc. of Arts, xxi., 428; xxii., 209
- „ as dyed by the Greeks. Thomson's Annals, ix., 134
- „ Schoerbing upon methods used in 1803. Nicholson's Journ., x., 128, from Van Mon's Journ., No. 15

- Turkey Red**, Hausmann's method of dyeing. *Ann. de Ch.*,
xlviii., 243
- „ Society of Arts pay £150 for the receipt of, and
communicate it to the public. See *Trans.*, xlv., 24
- „ Jenny upon the practice and theory, memoir for
which a medal of the first class was awarded
by the Mulhouse Society. *Bull. de Mulh.*,
xxxviii., 747
- „ Müller's test for goodness and stability. *Technol.*,
xxxiii., 61, from *Chem. Centralbl.*, 1872, No. 6
- „ Dyeing of in Greece. *Ann. de Ch.*, xxxi., 195
- „ Pelouze on the oils used for. *Chem. Gaz.*, xiv.,
317, from *Comptes Rendus*, 1856, p. 1196
- „ Wallace upon fires arising from oiled goods. *Brit.*
Assoc., Oxford, 1860; *Chem. News*, ii., 160
- „ Mercer and Greenwood's prepared oils for, patent
March 15th, 1852. *Chem. Gaz.*, x., 469
- „ Müller on recovery of the tartaric and oxalic acids
used in discharging. *Chem. Soc. Journ.*, xxiv.,
172, from *Chemisch. Centralbl.*, 1871, p. 134
- „ Townsend and Walker's patent for hyposulphite
and sulphite of alumina in dyeing. *Technol.*,
xxiii., 236
- „ Wartha on action of petroleum oils upon. *Chem.*
News, xxii., 130, from *Berech. Deutsch. Ch.*
Gessel., No. 12, 1870
- „ preparations for. *Ann. de Ch.*, xii., 200; xxvi.,
205; xxxi., 195
- Turmeric**, Schlumberger on action of boric acid upon. *Bull. de*
Mulh., xxxv., 193
- „ Daube upon the colouring principle of. *Chem. News*,
xxii., 154
- „ Köchler upon. *Chem. News*, xxii., 84, from *Berich.*
Deut. Gessel., No. 13, 1870; *Chem. Soc. Journ.*,
xxiv., 152
- „ colouring matter of. *Ann. de Ch. et Ph.* (3) viii., 380
- Ultramarine**, Zuber and Schlumberger. *Bull. de Mulh.*, xxii., 38
- „ Schützenberger upon natural and artificial. *Bull.*
de Mulh., xxxv., 97

- Ultramarine,** Röhrig upon. *Chem. News*, xvi., 188
 „ Dollfus and Goppelsroeder upon. *Bull. de Mulh.*,
 xlv., 193
 „ Stein upon. *Chem. Soc. Journ.*, xxiv., 166, from
Journ. für Prakt. Ch. (2), iii., 39
 „ Morgan upon. *Chem. News*, xxvii., 39; *Ulgren*,
 xxvii., 51
 „ Gentele upon. *Chem. Gaz.*, xvi., 16
 „ observations upon. *Chem. Gaz.*, i., 24; iii., 238;
 iv., 401; *Technol.*, iii., 400; vi., 491; *Ann. de*
Ch. et Ph., xxxvii., 409; xl., 439
 „ Benner upon the fineness of commercial samples.
Bull. de Rouen, ii., 37
 „ Hoffmann upon quantity of sulphur in various.
Bull. de Mulh., xlvi., 142

- Unwoven Goods.** The following patents, not referred to pre-
 viously, may be consulted as to apparatus
 for washing, bleaching, and dyeing un-
 woven goods, as yarns, hanks, warps,
 skeins, cops, etc. Patents for printing un-
 woven goods are mentioned vol. i., p. 128
- „ „ Mallison: Dyeing in cop or hank, No. 1106,
 May 18th, 1858
 „ „ Holden: Yarn apparatus, No. 2332, Oct.
 13th, 1859
 „ „ Pickstone and Bacon: Dyeing, etc., No.
 1333, May 30th, 1860
 „ „ Goddard: Black dye on doubled yarns. No.
 96, Jan. 13th, 1861
 „ „ Marshall: Vacuum apparatus, No. 286, Feb.
 2nd, 1861
 „ „ Kirkham and Henson: Cop bleaching, No.
 492, Feb. 24th, 1862
 „ „ Eastwood: Wringing hanks, No. 1509, May
 19th, 1862
 „ „ Davies (Tulpin): Washing skeins, No. 2365,
 Aug. 26th, 1862
 „ „ Whittaker and Tongue: Rovings, No. 367,
 Feb. 10th, 1863

- Unwoven Goods.** Veret: Skein dyeing, No. 1507, June 17th, 1864
- ” ” Stobs and Pollock: Hank drying, No. 2661, Oct. 17th, 1864
- ” ” Jerasson: Bleaching yarns, No. 2773, Nov. 8th, 1864
- ” ” Holms: Warp dyeing, No. 3226, Dec. 28th, 1864
- ” ” Mallison: Warp mordanting, No. 490, Feb. 22nd, 1865
- ” ” Akeroyd: Reserving warps for checks, No. 617, March 4th, 1865
- ” ” Gauteret: Yarn dyeing, No. 718, March 14th, 1865
- ” ” Ferrie and others: Hank dyeing, No. 1193, April 29th, 1865
- ” ” Pollock and Stobs: Yarn washing, No. 2044, Aug. 7th, 1865
- ” ” Smith and Schofield: Yarn washing, etc., No. 2113, Aug. 16th, 1865
- ” ” Vigoureux: Thread washing, No. 2126, Aug. 17th, 1865
- ” ” Mallison: Cop dyeing, No. 314, Feb. 1st, 1866
- ” ” Barlow: Threads and yarns, No. 468, Feb. 14th, 1866
- ” ” Mather: Hank washing, No. 570, Feb. 23rd, 1866
- ” ” Newton: Dyeing apparatus, No. 1440, May 22nd, 1866
- ” ” Stephen: Apparatus for moving, No. 2465, Sep. 25th, 1866
- ” ” Johnson and Giles: Hank drying, No. 1389, May 10th, 1867
- ” ” Crossley: Washing after steaming, No. 165, Jan. 15th, 1868
- ” * ” Mc.Leod: Yarn washing, No. 629, Feb. 25th, 1868
- ” ” Mc.Leod: Yarn apparatus, No. 1968, June 17th, 1868

Unwoven Goods.	Ingham : Warp dyeing, No. 2535, Aug-13th, 1868
”	” Matheson : Connecting hanks, No. 3480, Nov. 16th, 1868
”	” Hirsch : Yarn dyeing, No. 3689, Dec. 4th, 1868
”	” Dargue : Dyeing apparatus, No. 1548, May 27th, 1870
”	” Miller : Yarn dyeing, No. 1840, June 28th, 1870
”	” Mc.Leod : Liquoring apparatus, No. 392, Feb. 16th, 1871
”	” Mc.Leod : Dyeing apparatus, No. 494, Feb. 24th, 1871
”	” Stewart : Washing yarns, No. 1470, June 20th, 1871
”	” Ripley : Spray dyeing, No. 283, Jan. 30th, 1870
”	” Cooke : Dyeing apparatus, No. 1943, June 27th, 1872
”	” Todd : Yarn dyeing, No. 1974, June 29th, 1872
”	” Mc.Farlane : Dyeing apparatus, No. 2384, Aug. 10th, 1872
”	” Hacking : Yarn dyeing, No. 2858, Sep. 28th, 1872
”	” Wilkinson : Scouring yarns, No. 2961, Oct. 8th, 1872
”	” Wilkinson : Dyeing yarns, No. 3597, Nov. 29th, 1872
”	” Fillingham : Beaming for printing, No. 3669, Dec. 4th, 1872
”	” Carmichael : Bleaching yarns, No. 72, Jan. 7th, 1873
”	” Wirth : Washing yarns, No. 1332, April 10th, 1873
”	” Dargue : Hank dyeing, No. 2036, June 7th, 1873
”	” Johnson : Slubbing dyeing, No. 3601, Nov. 5th, 1873

- Unwoven Goods.** Mallison: Dyeing yarns, No. 3993, Dec. 4th, 1873
- „ „ Baerlein: Yarn apparatus, No. 4014, Dec. 5th, 1873
- „ „ Gottheil: Warp dyeing, No. 36, Jan. 2nd, 1874
- „ „ Kennedy: Dyeing in spinning, No. 2213, June 25th, 1874
- „ „ Sauvée: Frame for dyeing, No. 2982, Nov. 5th, 1874
- Uranium,** Davies on its powers as mordant. Trans. Soc. of Arts, *xlviii.*, 47
- Uric Acid,** Wohler and Liebig upon. Ann. de Ch. et Ph., *lxviii.*, 225
- Urine,** Cook's patent for treating, No. 2342, Sep. 23rd, 1799
- Vanadium,** Hommey upon aniline black by, upon woollen and mixed goods. Bull. de Rouen, *iv.*, 263
- „ Witz upon use of in aniline black. Bull. de Rouen, *iv.*, 310
- Violet,** Nuremberg, appears to be a phosphate of manganese. Technol. *xxx.*, 243
- Viscometer** for testing gums. Technol. *v.*, 14, 23
- Washing.** Auchinloss' machine. Technol., *xxii.*, 199
- „ Witz and Brown's machine. Bull. de Mulh., *xxxiv.*, 49
- „ various machines. Bull. de Mulh., *xxix.*, 506; *xxx.*, 564
- Water,** Dupasquier on bicarbonate of lime in: Chem. Gaz., *v.*, 354; Comptes Rendus, *xxiv.*, 808
- „ Wagner's treatment of hard waters. Bull. de Mulh., *xxxiii.*, 272
- „ Clark's paper on testing hardness. Chem. Gaz., *v.*, 100
- „ Laschi's patent to ascertain quantity of lime to be added to soften, No. 2199, August 5th, 1862
- „ Pearson's patent for using distilled in bleaching, etc., No. 1583, June 15th, 1871
- „ Paget's patent for purifying, etc., No. 3953, December 2nd, 1873
- „ Hunt's patent for purifying by spent soap liquors, No. 584, March 4th, 1871

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Wongahy, Stein upon; yellow contained in seed vessels of a Batavian plant, similar in properties to annatto. Chem. Gaz., viii., 73, from Journ. für Prakt. Chem., December 1st, 1849; Technol., xi., 355

Wool Washing, etc. The following patents may be consulted upon the apparatus and materials used in treating unspun wool.

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| ” | ” | ” | Pasquier, for apparatus, No. 1269, May 23rd, 1859 |
| ” | ” | ” | Dawson, for dyeing black, No. 1528, June 23rd, 1860 |
| ” | ” | ” | Pimont, for drying in flock, No. 22, Jan. 4th, 1861 |
| ” | ” | ” | Compte and Prevost, washing, No. 588, March 8th, 1861 |
| ” | ” | ” | Plantrou, washing and scouring, No. 2371, Sep. 22nd, 1861 |
| ” | ” | ” | Illingworth, washing, No. 3077, Nov. 15th, 1862 |
| ” | ” | ” | McNaught, washing, No. 3274, Dec. 6th, 1862 |
| ” | ” | ” | Holden, washing, No. 3395, Dec. 18th, 1862 |
| ” | ” | ” | Chaudet, dyeing slivers, No. 1243, May 17th, 1864 |
| ” | ” | ” | McNaught, washing apparatus, No. 3122, Dec. 16th, 1864 |
| ” | ” | ” | Hughes, drying, No. 255, Jan. 28th, 1865 |
| ” | ” | ” | McNaught, washing and drying, No. 281, Feb. 1st, 1865 |
| ” | ” | ” | Crabtree, washing apparatus, No. 1032, April 11th, 1866 |
| ” | ” | ” | Petrie, washing apparatus, No. 577, Feb. 24th, 1866 |
| ” | ” | ” | Phillipe, use of carbonate of ammonia, No. 257, Jan. 30th, 1867 |

- Wool Washing, etc.** Norton, drying apparatus, No. 1486,
May 18th, 1867
- ” ” ” Petrie, washing apparatus, No. 666, Feb.
27th, 1868
- ” ” ” Petrie, washing apparatus, No. 874, Mar.
14th, 1868
- ” ” ” Heyl, sulphide of carbon for, No. 1887,
June 28th, 1867
- ” ” ” Petrie, washing and dyeing, No. 3617,
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- ” ” ” Mc. Naught, washing and drying, No. 1511,
May 25th, 1870
- ” ” ” Toepler, amyl alcohol for, No. 1123, April
18th, 1870
- ” ” ” Simonin and Coffin, washing, etc., No.
1219, April 27th, 1870
- ” ” ” Toepler, naphtha vapours for, No. 2743,
Oct. 18th, 1870
- ” ” ” Thomas, sulphide of carbon for, No. 354,
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- ” ” ” Cochrane, apparatus, No. 389, Feb. 15th,
1871
- ” ” ” Rydill, dyeing and staining, No. 2752,
Oct. 17th, 1871
- Wool.** Leuch's essay upon wool bleaching. Technol., xxii., 125
- ” Elsner on various kinds of, microscopical. Technol.,
xxvii., 89
- ” Damsthorpe's apparatus for washing. Technol., xxvii., 583
- ” Norton's apparatus for drying. Technol., xxi., 89
- ” dyeing Prussian blue upon. Chem. Gaz., x., 414, from
Muster. Zeit., 1851, No. 3
- ” Kober's patent for use of bichromate in dyeing. Chem.
Gaz., ii., 226
- ” Peissert upon action of bichromate in dyeing. Technol.,
xxi., 131
- ” Ettel's mordant for dyeing. Technol., xxiii., 359
- ” Lightfoot, treating with chlorine to enable it to take
aniline black. Chem. News, xiv., 58
- ” Guillouet on dyeing Prussian blue upon. Chem. Gaz.,

- x., 144; *Must. Zeit.*, 1851, No. 3, from Schweiz. *Gewerbebl.*, xi., 119
- Wool**, action of chemical agents upon. *Ann. de Ch.*, x., 133; xxi., 28; xxx., 215
- Yellow Colour.** Buchner and Phipson on yellow from *Rhamnus frangula*. *Chem. Gaz.*, xvi., 344
- „ „ from *Gardenia grandiflora*. *Chem. Gaz.*, xvi., 331. *Trans. Vienna Acad.*, xxix., 1
- „ „ from Chinese yellow pods, probably same as above. *Stein. Chem. Gaz.*, xi., 221; also Van Orth, xiii., 28, from *Trans. Vienna Acad.*, xiii., 590
- „ „ Belhomme upon, from *Paulownia imperialis*. *Chem. Gaz.*, xvii., 113
- „ „ from saffron, for fancy articles. *Technol.* iv., 447
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